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ERRATA

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Page 365, line 38 for 41,000 k.v read as 41,000 v

Page 372, line 27 for $\frac{e^{-h\nu^0/kT} + 1}{e^{-h\nu^0/kT} - 1}$ read as $\frac{e^{h\nu^0/kT} + 1}{e^{h\nu^0/kT} - 1}$

Page 389, Figure 1 for Scale $\frac{1}{2}$ full size read as scale 1/6 full size

Plate XXIV, Figure 8 for 4346 read as 4046° A.

Pages 415 20, for Hexamethyl-tetramine read as hexamethylene-tetramine.

Page 431, Table III, line 6 for (400) reflections read as 2 (200) reflections.

Page 431, Table III, line 6 for (600) reflections read as 3 (200) reflections.

ERRATA

Vol XIV, No 3, Section A, 1941

Page 313, para 2, line 5 for quadric " Σ_1 " read quadric " Σ ,"

„ 313, „ 4, „ 3 for " $2 U_{il}$ " read " $2 U_{lp}$ "

„ 313, „ 4, „ 4 for " V_i " read " U_i "

„ 315, „ 1, „ 3 for " ψ_2 " read " ψ_a "

„ 315, „ 1, „ 2 in the equation, for " $-\psi_a (a S_{18} + S_{1a})$ "
read " $-\psi_a (a S_{18} + d S_{1a})$ "

„ 315, „ 2, „ 2

for " $2 S_{1A} - \frac{\partial S_i(V)}{\partial A}$, , , $\psi_A a A \pm b B +$ "

read " $2 S_{1A} \equiv \frac{\partial S_i(V)}{\partial A}$, , , $\psi_A \equiv a A \pm b B +$ "

„ 315, line 2 from bottom for " $P'\mu$ w r t " read " $\mu P'$ w r t. "

THE LUMINESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN DIAMONDS: PART III. ABSORPTION

BY P G N NAYAR

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE early work of Miller (1862) on the transparency of various bodies, and the refractive index determinations of diamonds by Peter (1923) give indications that some diamonds are more transparent than others to ultra-violet light. This question was the subject of an extensive investigation by Robertson, Fox and Martin. In a paper entitled "Two types of diamonds" in the *Transactions of the Royal Society* and a further communication in the *Proceedings of the Royal Society* (1936), these authors set forth evidence collected from the examination of a large number of crystals that diamonds fall into two distinct classes as regards their property of ultra-violet absorption. Crystals of type I, which are of more common occurrence, were found by them to be opaque to ultra-violet light beyond 3000 Å, while crystals of type II, met with only rarely, were found to transmit light freely up to 2250 Å. These authors also found that in the region just preceding that of complete absorption, there were present a number of narrow discrete absorption bands. In the common type they reported 8 absorption bands between 3000* and 3300, while in the rare type they observed a selective absorption with faint unresolved bands between 2330 and 2350.

In the near ultra-violet region, Walter (1891) had investigated the absorption of diamonds using sunlight as source. His observations did not extend very far in the ultra-violet because of the use of a glass spectrograph, but in the violet region he found a sharp absorption line at 4155, and evidence of a general absorption of unspecified wave-lengths on the short wave-length side of this line. According to him, this band was strongest in

*The figures here and in subsequent parts of the paper refer to wave-lengths in Å U.

the case of a yellow specimen and weak in stones coloured red, green or brown. However he has stated that this band at 4155 was present in all colourless crystals as well, of over a carat (or more properly, of sufficient thickness of absorbing material). In addition a very faint band at 4710 was noted by him. In the work of Robertson *et al* it has been mentioned that only in one case were they able to observe the absorption at 4155, and because they did not notice this band in the other crystals investigated by them, they dismissed it as not normal to diamonds.

In two previous papers on diamond referred to as Part I and Part II in this paper, the author (1941) has presented evidence to the effect that an emission band at 4156 is of fundamental importance in the fluorescence and phosphorescence of diamond and that it occurs with striking variations in its intensity in different crystals. An absorption in this region therefore is of particular interest, and the conflicting results obtained by Walter and Robertson and others require a re-examination. Further, the wide variation of intensities of fluorescence in crystals of as much as 10,000 : 1 in the collection of crystals reported in Part I by the author, gives an indication that differences in absorption ought to be considered on the basis of the fluorescence of the crystals and not in regard to their colour as had been attempted by Walter.

The whole question of transparency in the ultra-violet and the structure of the absorption bands was therefore subjected to a careful investigation, using suitable technique. The studies revealed that the earlier work was far from complete in regard to the number of absorption bands, and had completely failed to recognise the significance of absorption frequencies and their intensity variations in relation to the fluorescence of the crystals. The present paper describes the details of the new results obtained by the author in regard to absorption of light, while the two earlier papers referred to above bearing on the subject have already dealt with the emission of light from diamonds as fluorescence and phosphorescence.

2 *Transmission in the Ultra-violet*

The specimens in the collection of crystals used in this work have been numbered and described in a table in Part I (p 485). Therein it has been mentioned that some of the diamonds were in the form of flat plates of thicknesses varying from 76 μ m upwards. These plates were specially useful for studying the extent of transmission in the ultra-violet. A water-cooled hydrogen discharge tube with a quartz window, running on 3000 volts 300–500 ma, provided a very intense source of continuous spectrum

extending to 1800 Å The diamonds were fixed so as to completely cover small apertures in metal plates, and the light passing through the crystals was focussed on the slit of a Hilger medium quartz spectrograph using quartz lenses

All the crystals were systematically tested and were found to belong to the class designated type I by Robertson, in view of the fact that free transmission in the ultra-violet did not extend up to 2250 Considering them as type I or the common type of crystals, the results obtained are in agreement with the earlier work to the extent that very strong absorption sets in at about 3000 Å, but differs in respect of the completeness of absorption at 3000 Å Actually light is found to be weakly transmitted much farther into the ultra-violet, up to about 2700 as could be seen by the use of comparatively thin sections of under 1 mm With thicker specimens of 3 or 4 mm, the cut off at 3000 appears very sharp and gives the impression of total absorption

The extent of absorption in this region is illustrated in Fig 1 (Plate I) where the spectra of light passing through different thicknesses, with graded exposures are shown With the plate of 76 mm thickness, the absorption can be seen to extend to 2700 while in the last picture of the group, with a thickness of 2.35 mm, the absorption appears to be complete at about 3000. Several narrow bands are also present in this region and these are dealt with in the next section.

3 Discrete Absorption Bands

In the region just preceding complete absorption on the long wave-length side, Robertson *et al* had observed some narrow bands A careful examination of the plates taken with a series of graded exposures showed that similar bands were present in the region of weak transmission obtained with thin plates as described in the previous section Of these the first two at 2715 and 2770 are extremely faint and are hardly noticeable in the reproduction of the spectra The next one at 2845 is more prominent and is followed by two others at 2950 and 2975 The region between 3030 and 3300 is the one covered in detail by Robertson. Since in this region the general absorption is not strong, larger thicknesses could be employed with advantage. The flat plates in the collection were gripped by metal plates, and the light after being absorbed by the full length of the crystals (maximum 12 mm) was studied as before The bands could be recorded very strongly and a few representative photographs are reproduced in Fig 2 (Plate I) All the bands reported earlier except a doubtful frequency at 3242 were confirmed,

and in addition it was found that three more similar bands were present at 3340, 3383 and 3451

The region beyond these bands towards the visible was found by Robertson to be free from any absorption except for a rare instance of a band at 4156. As mentioned already Walter's work gives indications of a general absorption in this region. The spectra obtained with the present collection of crystals showed that actually there were present a set of discrete, though, broad and diffuse bands in the region beyond 3600 up to 4156, at which wave-length a sharp and strong band could be seen without difficulty in all cases. These bands can be seen in Fig 2 (Plate I). Since the hydrogen discharge lamp has a number of lines in this region, an over-run tungsten filament lamp was also used for investigation of the details of these bands.

These diffuse bands and the band at 4156 were remarkable in that, though they could be detected in every crystal, they were exceptionally strong in some cases. This aspect of the question is dealt with in a subsequent section, but since the existence of these frequencies is quite general, the frequencies are included in the summarised table of all the observed absorption bands given below

A very weak and diffuse band in the visible region at 4730 corresponding to one at 4710 reported by Walter was found in two cases. Both these crystals were coloured yellow, and in other crystals they could not be detected under the most favourable conditions of thickness of absorbing material and source of light. This absorption is therefore considered unusual and probably connected with the yellow colour, and is therefore not included in the table.

The narrow bands referred to above were roughly 5 Å in breadth and only in a few cases were they strong enough to be measured with a micrometer. The wave-lengths of the weak bands estimated by comparison with the iron-arc spectrum taken side by side are correct to only 5 Å, and the values are in reasonable agreement with available earlier values which are also given in the table. The diffuse bands on the other hand extend over 20 to 30 Å and the wave-lengths of the intensity peaks are of lesser accuracy. Since all the bands could not be recorded in one and the same picture, it was not possible to arrive at a reliable estimate of the relative intensity of the bands. Moreover, the relative intensity of different regions was found to be variable in different crystals and the relative intensities indicated in Table I are valid only in respect of neighbouring lines.

TABLE I

Visible and Ultra-violet Absorption Frequencies in Diamond

Walter	Robertson <i>et al</i>	Author		
AU.	20°C AU	—180°C AU.	25°C AU.	25°C cm. ⁻¹
			2715 (v f)	36820
			2770 (v f)	36090
			2845 (m)	35140
			2950 (f)	33890
			2975 (v f)	33600
	3037		3030 (m.)	32990
	3067		3060 (m)	32670
	(3085)*	3070	3075 (f)	32510
	3157	3154	3157 (s)	31670
	3179	3172	3175 (m)	31490
	3204	3200	3205 (m)	31190
	3242*			
	3302	3300	3306 (m)	30240
			3340 (f)	29930
		3380	3383 (m)	29550
		3450	3451 (m)	28970
		(3680)	3680*(v f d)	(27170)
		3750	3760 (m)	26590
		3840	3850 (m)	25970
		3950	3950 (m)	25310
		4040	4041 (m)	24740
		4153	4156 (s sh)	24054
General absorption				
4155				

*Very faint frequencies found only at liquid air temperature In the table brackets indicate extremely faint frequencies whose measurements are uncertain The sharpness and intensity are represented by the following abbreviations.—v.f., very faint, f, faint; m, medium, s, strong, p., diffuse; and sh., sharp.

4 *Influence of Temperature*

The effect of temperature on the absorption bands was studied at a low temperature by cooling the crystal with liquid air, and at higher temperatures up to 300° . For this purpose a crystal of suitable size was set in a copper rod, which was cooled down by immersion in liquid air. To prevent ice formation on the crystal during exposure, the end holding the crystal was enclosed by a long glass tube with quartz windows. For higher temperatures the rod was heated electrically and the temperature reached by the crystal was measured by a thermo-couple.

The general effect of cooling the crystal is to increase the absorption in the whole region. The bands become considerably sharper at liquid air temperature and shift towards the ultra-violet to the extent indicated in Table I. The diffuse bands in the region between 3000 and 4000 become sharper at the edges and show the structure of the individual bands, the changes being quite parallel to the behaviour of the corresponding fluorescence bands.

The investigations were limited to only one thickness of crystal and the entire region could not be investigated by the use of different absorbing thicknesses as was possible at room temperature. The low temperature pictures were mainly helpful in confirming the presence of the diffuse band at 3680 and showing the finer details of the other diffuse bands.

The first two pictures in Fig. 3 (Plate II) show the spectra taken at room temperature and at liquid air temperature, side by side, using a Hartmann diaphragm with the same exposure time. The general increase of absorption and the shift of the bands can be seen therein. The third picture is also at liquid air temperature, but with a greater exposure to bring out the bands which are not clear in the other picture.

At high temperatures the bands lose their sharpness and intensity, and at 300° no sign of the discrete bands could be observed in any region. The behaviour of the 4156 band in absorption when the temperature is raised in small steps is illustrated in Fig. 4 (Plate II) and shows the shift and unsymmetrical diffusion of the band which is parallel to the behaviour of this band in fluorescence described in Part I.

5. *Absorption Intensity in Relation to Fluorescence*

The fact that the absorption band at 4156 is identical in wave-length with the principal fluorescent band suggests naturally that a basis for the variation of intensity of this absorption band indicated earlier, is to be sought for in the difference in fluorescence of the crystals. It was seen from

the spectra of the crystals in the collection, that considering nearly equal thicknesses of crystals employed, the specimens showing strong fluorescence also showed strong absorption at 4156. This is clearly illustrated in the case of the spectra of D_1 and D_2 taken with nearly equal absorbing thicknesses. These two diamonds have been compared quantitatively in respect of their fluorescence intensities in Part I, where it has been shown that D_2 is about 100 times stronger than D_1 in fluorescence. In Fig 5 (Plate III) where the absorption spectra are reproduced, it can be seen at once that D_2 shows considerable absorption at 4156 while in the case of D_1 the intensity is negligible. The diffuse absorption bands also behave in exactly the same way as the 4156 band, showing strong absorption or weak absorption according as the crystal is highly fluorescent or weakly fluorescent.

The group of sharp bands at the other extreme of ultra-violet transmission of which the one at 3157 is the strongest, behave in a different fashion from the above. A careful examination of the spectra of all the diamonds showed that though these bands are not affected to the same extent as the diffuse bands, there is a definite dependence of the sharpness and intensity of these on the fluorescence but in the opposite direction. The absorption spectra of the strongly fluorescent D_2 and weakly fluorescent D_1 with nearly the same thickness already referred to in Fig 5, show that the narrow bands are a little more diffuse and fainter in the strongly fluorescent specimen. In the crystal D_1 which showed the strongest fluorescence and phosphorescence in the whole collection, a special search failed to reveal these bands with anything of their usual intensity and sharpness. Even at liquid air temperature where the bands increase in strength and sharpness only the vaguest indication of their presence was seen in the plates, showing that the factor which gives high fluorescence intensity has also a tendency to suppress these absorption bands.

The group of lines between 3300 to 3450 however were seen in all the pictures with a slightly higher intensity in fluorescent crystals, but appeared to be more diffuse in such cases.

The position regarding the influence of the fluorescing power of the crystals on absorption can therefore be summed up as follows. The band at 4156 and the diffuse bands are *directly correlated in intensity with fluorescence* being strongest in the case of the most highly fluorescent crystals and weakest in the case where the fluorescence is negligible. The sharp band in the ultra-violet at 3157 and the neighbouring bands however are *influenced in the opposite way, but to a lesser extent*, being sharp and strong with weakly fluorescent crystals and fainter and more diffuse with highly

fluorescent specimens. The intermediate bands between 3300 to 3450 become slightly more diffuse when the fluorescence is very strong but the intensity appears to be a little more in such cases. The failure of Robertson *et al* to observe absorption on the long wave-length side of 3306 is intelligible when it is remembered that they specifically mention in their paper that the diamonds used by them were, as they supposed, free from fluorescence. In such cases of extremely weak fluorescence, these bands beyond 3300 can be detected only by using thick absorption layers. But there is no doubt that these frequencies appear in all diamonds and the behaviour as regards intensity is parallel to that of the fluorescence intensity.

Anomalous dispersion in the region of absorption—Since the highly fluorescent crystals exhibit very strong absorption at 4156, an attempt was made to study the dispersion in this region to see whether the crystal would show the so-called anomalous dispersion in the region of absorption. The well-known technique of crossed spectra was made use of for this purpose. Using a prismatic edge of a fluorescent diamond, the spectrum of a distant source of white light was thrown on the slit of a spectrograph. The diamond dispersed the light vertically along the slit, while the spectrograph prism dispersed it horizontally. Some slight evidence of an effect of anomalous dispersion was observed, but could not be considered conclusive owing to the imperfection of the dispersing edge of the diamond. An investigation with proper material would be worthwhile as it might be possible to estimate the number of dispersion electrons on the lines of the familiar experiments on sodium vapour and hydrogen. It is hoped to take up this question later.

6. *Relation of Absorption to Fluorescence*

The absorption and fluorescence frequencies coincide exactly at 4156. On looking at the diffuse absorption band system it is apparent that it appears symmetrical in its distribution about the 4156 band to the fluorescent bands on the long wave-length side. That such is the case is found on putting down the differences in frequencies from the 4156 band, when it is seen that every band in fluorescence has a corresponding absorption band in the ultra-violet displaced from 4156 by the same wave-number shift. In Table II below, the room temperature values of the frequencies in both absorption and fluorescence are given side by side with their differences from the principal band. The fluorescent bands are numbered as in Part I. In connection with the principal fluorescent bands given in Table II, it should be remarked that the finer details of each of these bands are reproduced also in absorption. Proceeding from the principal line at 4156

TABLE II

Fluorescence and Absorption Frequencies in Wave-numbers (room temp.)

Band No.	Fluorescence cm ⁻¹ .	Difference	Absorption cm ⁻¹	Difference
I	24050 sharp	.	24050 sharp	.
II	23520 edge 23370 peak	580 680	24580 edge 24740 peak	580 690
III	22790 peak 22700 edge	1860 1850	25310 peak 25410 edge	1960 1980
IV	22150	1200	25970	1980
V	21530	2520	26590	2540
			(27170)	(8100)

(24050 cm⁻¹), the second band in fluorescence starts with a somewhat sharp edge and the corresponding band in absorption has likewise a sharp edge. The third band is narrow compared with the second and has a double structure which is reproduced exactly in absorption. The remaining bands get progressively diffuse but within the limit of uncertainty involved in the measurements of the peaks, the wave-number shifts are identical. The last absorption band at approximately 3680 Å, corresponds to the region of continuous spectrum in fluorescence in which there is a perceptible concentration of intensity between 4800 and 4900 Å.

The faint intermediate bands in fluorescence also have absorptions in their corresponding places. They are not included in Table II since the measurements were found to be too difficult to permit of any accuracy.

The remarkable mirror-image symmetry of the system of absorption and fluorescence bands seen from the above table, is brought out in a striking way by photographing the fluorescence and absorption side by side using a Hartmann diaphragm. Such a picture is reproduced in Fig 6 (Plate III). Since this was taken with a glass spectrograph, the extreme ultra-violet bands are not included, but the exact coincidence of the emission and absorption bands at 4156, and the symmetrical distribution of the bands about this frequency are very well brought out. The higher dispersion in the ultra-violet exaggerates the displacements on that side; a representation of these bands on a wave-number scale is therefore given also in a chart of frequencies, elsewhere. The second picture shows the effect of raising the temperature to 180°. The absorption band at 4156

broadens and shifts corresponding to the broadening and shift of the fluorescent band. The bands on the whole get diffuse, but the mirror-image symmetry continues to be preserved.

7 *Relation to Infra-red Frequencies*

The frequency differences of the bands from the 4156 band found in both fluorescence and absorption in the last section come out as 690, 1260, 1920, 2540 and the last one approximately 3100. A search for the possible meaning of these figures showed that they bear a rough correspondence to certain infra-red frequencies found in diamond earlier by Robertson and others. Their work in this field is therefore worth a close examination.

The absorption by diamond in the infra-red had been investigated by Angstrom (1892), Julius (1893) and Reinkober (1911). The conflicting results obtained by the different authors especially in regard to absorption in the 8μ region led Robertson, Fox and Martin to make a detailed search for the absorption frequencies with a number of diamonds. These authors were able to confirm the presence of bands reported earlier in the regions 3μ , 4.1μ , 4.8μ and 8μ . The last mentioned band was remarkable, according to them, in its complete absence in some cases, and they were able to show that such crystals belonged to the type which is transparent to ultra-violet between 3000 and 2250.

The main difference between Reinkober's results and that of Robertson is the absence of any strong absorption in the 8μ region in the former's work. Robertson obtained an absorption of roughly 95% (neglecting loss due to reflexion) with a thickness of 1.08 mm while Reinkober's curve shows only minor fluctuations in this region of free transmission (about 70%) found by him, with a thickness of 1.26 mm. This is satisfactorily explained by Robertson as due to Reinkober's diamond being of the transparent type, as the 8μ band had been observed previously by Julius and Angstrom.

Another notable difference was a sharp fall of about 7% at 14μ in a region of 70% transmission noted by Reinkober which was not observed by Robertson.

In the chart on page 12 giving the energy levels in both absorption and emission, these infra-red frequencies are shown on the left hand side in wave-numbers, starting from the 4156 band. The bands have a number of subsidiary peaks which are shown by thick lines in the diagram.

Since all the crystals dealt with in this work are opaque to ultra-violet light beyond 3000, it is assumed that these crystals are in the class which

have an absorption at 8μ Reinkober's frequency at 14μ is included since it fits in with the other results

Since the diagram is on a wave-number scale a rough correspondence between the infra-red frequencies and the frequency differences of the ultra-violet bands is apparent. Neglecting the details of the diffuse bands, the mean wave-numbers given on the left hand side of the diagram agree approximately with the wave-number differences marked on the right hand side. These figures are collected together in the Table below:

TABLE III

Frequency difference from 4156 band		Infra-red frequency
Absorption	Fluorescence	
690	680	710
1260	1260	1290
1920	1900	2040
2540	2520	2480
(3100)		(3500)

All the bands are broad and diffuse, and the widths of the bands are sufficient to accommodate the discrepancy. Even considering this factor, it is not safe to presume that the agreement is exact, but the band to band correspondence of the fluorescence and absorption frequency differences on the one hand and the infra-red frequencies on the other, cannot possibly be accidental. It is therefore reasonable to assume that these infra-red energies of undetermined origin found in diamond are of significance in fluorescence also.

8. Explanation of the Mirror-image Symmetry of Absorption and Fluorescence

The chart in Text-fig. 1 summarises the results of the spectroscopically determined energy levels in diamond. From what has been described in the previous pages, it follows naturally that 4156 and the system of diffuse bands belong to a category different from the sharp bands. The latter bands are due to the levels in the crystal as a whole, as they have been observed in all crystals by Robertson and co-workers, as well as by the present author, irrespective of the fluorescence of the crystals which influences them only in a secondary way.

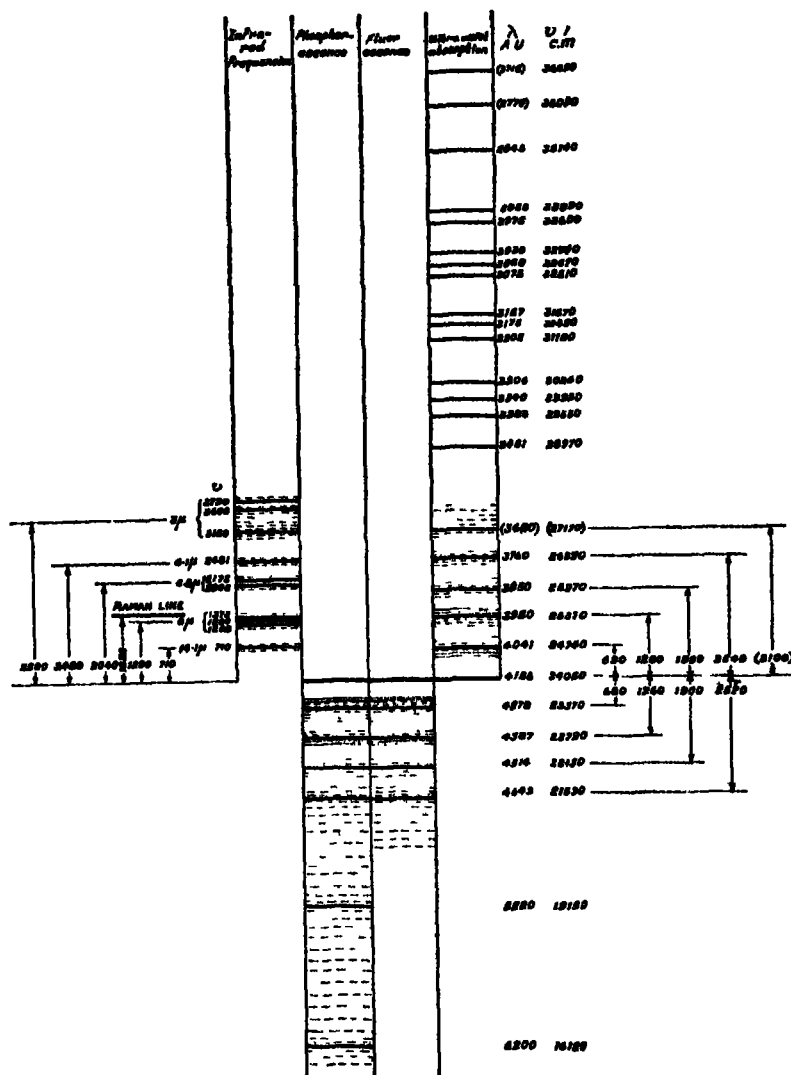


FIG 1

Energy Levels in Diamonds

The 4156 band is directly related to the fluorescence and arises from the principal electronic transition associated with fluorescence. The probable origin of the active centre responsible for this is discussed in a subsequent section, but taking the 4156 band as the principal transition, it is to be considered how the symmetry pattern of absorption and fluorescence can be explained.

The scheme of energy levels that can give rise to such a pattern can be illustrated by the usual type of energy level diagram shown in Text-fig. 2. The principal line with frequency 24050 cm^{-1} ($\lambda = 4156$) arises from a transition between an energy level E and a higher level E' , and can occur either

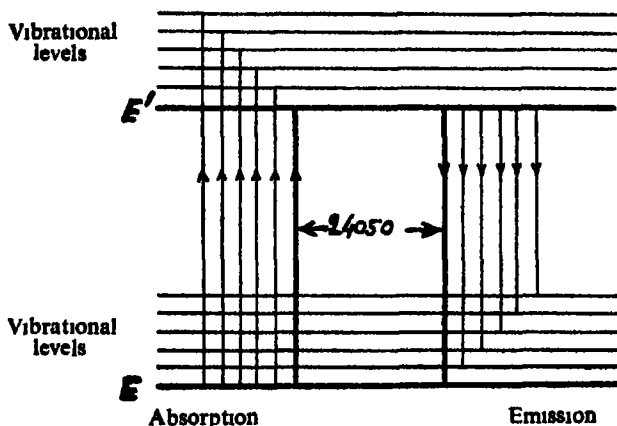


FIG 2

as an absorption or emission band of the same frequency. Associated with both levels we have further levels of the order of vibration frequencies. Transitions from the ground state of the lower level to the various upper levels would give rise to the system of absorption bands at 4156 and on the ultra-violet side of that band. But in emission, the transitions take place only from the ground state of the higher level E' as is seen from the fact that there are no emission lines on the short wave-length side of 4156. A satisfactory explanation, why jumps from the excited states of the higher level are not found can be had, if it is remembered that the absorption and emission process is confined to certain localised centres. As has been shown before, the higher vibrational levels are identical or nearly identical with the infra-red levels of the lattice, and because of this, it is reasonable to suppose that the energy after absorption is taken up instantaneously by the whole lattice. The active centre therefore, by the time it radiates, will be in the ground state of the higher level, and transitions involving higher frequencies than 24050 are not possible. In falling back, the quantum excites the vibrational levels of the lower state and gives rise to fluorescence of the same frequency or lower frequencies.

The relation of the absorption spectrum to that of fluorescence varies greatly in different substances. In alkali halide phosphors which have been very thoroughly investigated, the emission consists of narrow line-like bands in the visible and in the near ultra-violet, while the absorption which gives

rise to these lines, occurs very much farther in the ultra-violet in a number of comparatively broad bands. With uranyl salts, the absorption and emission spectra consisting of a number of narrow peaks of somewhat symmetrical pattern, overlap to some extent, showing the existence of transitions from excited levels of the higher state in emission. In chrome-activated phosphors the principal lines coincide in absorption and emission, but in general there is an overlapping of the absorption and emission spectra on the short-wave-length side of the principal lines. This is also true with respect to the great number of substances which give broad and diffuse spectra in luminescence and absorption.

In the coincidence of the principal frequency and the perfectly symmetrical distribution of combinational frequencies in absorption and fluorescence about the principal line, the case of diamond appears to be in a class by itself.

9 Probable Origin of Fluorescence in Diamonds

In looking for the origin of fluorescence in a substance the question of impurities in the sense of foreign atoms has to be considered first. The problem is one of difficulty since a concentration of impurity much smaller than what can be detected chemically can give rise to considerable luminescence effects. The evidence therefore has to be mainly spectroscopic, and is further complicated because the emission of the free atom is altered in frequency when imbedded in the lattice and lines due to transitions forbidden by selection rules in the free atom also are capable of making their appearance. So far, the successful detection of impurities in certain crystals has been made by the deliberate addition of impurities and identifying the spectrum with that in the unknown case. Obviously such a procedure is not possible with diamond and we have to be guided by information from other sources.

The chemically detected impurities in diamond, which occur in general as visible inclusions, are iron, titanium, magnesia, silica, and very often, graphite spots. There is no reason to suppose that any of the above elements can give rise to a single sharp line at 4156. Walter was led to suggest samarium as an impurity because rare earth salts are known to give sharp lines in fluorescence and absorption. The spectrum of samarium is now very well known, in absorption (Spedding, 1932) and in emission in its pure state as well as when it occurs as an impurity responsible for fluorescence (Pringshein, 1928; Randall, 1938). There is definitely no relation between the spectrum of samarium occurring as sharp lines between 5600 and 6500 and the fluorescent spectrum of diamond, nor could any resemblance be found to the spectra of other probable rare-earth elements.

It is now a widely recognised fact that the presence of foreign atoms is not a necessary condition for fluorescence, but that the atoms of the crystals themselves might, under certain circumstances, behave as active centres. Such conditions occur when there are interstitial atoms between fully occupied positions in the lattice, vacant positions and distortions of the lattice, or when electrons are transferred from one atom of the lattice to another. Disturbances of these types are definite possibilities in diamond considering the formation of the crystals at high temperature and pressure. Imperfect crystallisation is very common, the so-called "black diamonds" forming a gradation of imperfectly formed crystals ranging in hardness and density from those of diamond to those of graphite. One of the important results described in Part I was the fact that fluorescence in different crystals can vary to an enormous extent but that the 4156 band was present in all cases. The strength of this band, whether found in fluorescence or absorption was also shown to be entirely independent of the colour or visible inclusions in the crystals. It is therefore thought extremely improbable that any impurity, unless it be carbon itself, could be present in all crystals and by its variations of concentration give rise to the extreme differences found between the specimens. On the other hand, in view of the evidence for imperfect crystallisation, the wide variation of intensities can be satisfactorily accounted for on the supposition that lattice defects of the type indicated earlier are present in varying degrees in different diamonds.

10 Absorption in Relation to Electronic Structure

The electronic levels in crystals have in recent years been worked out in a few cases on the band theory of solids. The discrete levels in free atoms become spread out into bands when the atoms are bound together by crystalline forces and phenomena like absorption, conductivity and luminescence can be explained in a general way according to the filling by electrons of various energy bands. In connection with the investigation described in this paper, it is necessary to draw attention to a calculation of the energy states of diamond made by Kimball (1935), which seems to have been accepted as correct, at least as far as it applies to the ideal diamond lattice. According to this author the $2s$ and $2p$ levels of the carbon atom become spread out into broad bands in diamond, of which, the lower level is completely filled. The scheme of levels given by Kimball does not show any possibility of absorption of light in diamond, as the transition from the lower filled band to the band lying above it would require more energy than the ionisation potential of carbon. That the experimental facts are entirely otherwise has been shown in the course of this paper. Actually there is strong absorption up to 3000 Å in the ultra-violet and numerous

discrete bands in one type of diamond, and in another type, according to Robertson, absorption in the region of 2250 Å. These observations can only be explained by assuming that diamonds do not conform to the geometrically ideal structure, but that there are certain well-defined types of lattice disturbances which bring about a modification of the electronic levels. Between the 2s and 2p bands as present in the ideal lattice, the existence of subsidiary levels of the order of 3 to 4 e.v. are definitely indicated, and it is hoped that the experimental values will be of help in making a recalculation of the energy states.

It is necessary to stress that imperfections of a very slight nature are sufficient to bring about such changes. The alkali halide crystals are instructive examples of how slight disturbances of the lattice give rise to new intermediate levels. These crystals are normally completely transparent to the entire visible and ultra-violet up to the Schumann region, but lattice imperfections deliberately brought about by suitable heat treatment causes entirely new absorptions to appear.

Information already available from other sources like light-scattering, infra-red and X-ray structure also support these ideas. It is proposed to discuss these results with further experimental observations later on.

The author is thankful to Prof. Sir C. V. Raman for the loan of the crystals and for helpful advice and suggestions in this work.

11 Summary

This paper deals with the absorption of light by diamonds in the visible and ultra-violet regions, and is to be regarded as a continuation of earlier investigations on luminescence having a direct bearing on the results of this paper.

The absorption in the ultra-violet in all the crystals was found to be almost complete at about 3000 Å, but a weak transmission was observed up to 2700 Å. The spectrum shows narrow line-like bands extending from 2700 to 3400 together with a system of diffuse bands extending from 3600 to longer wave-lengths terminating in a sharp and intense band at 4156.

All the bands were found to sharpen and shift towards the ultra-violet at low temperatures. At higher temperatures they become progressively diffuse and practically disappear at 300°.

In the region of narrow bands, several new frequencies have been found in addition to those reported earlier by Robertson, Fox and Martin. The factor which is responsible for strong fluorescence in some crystals is found to have a tendency to suppress the narrow bands.

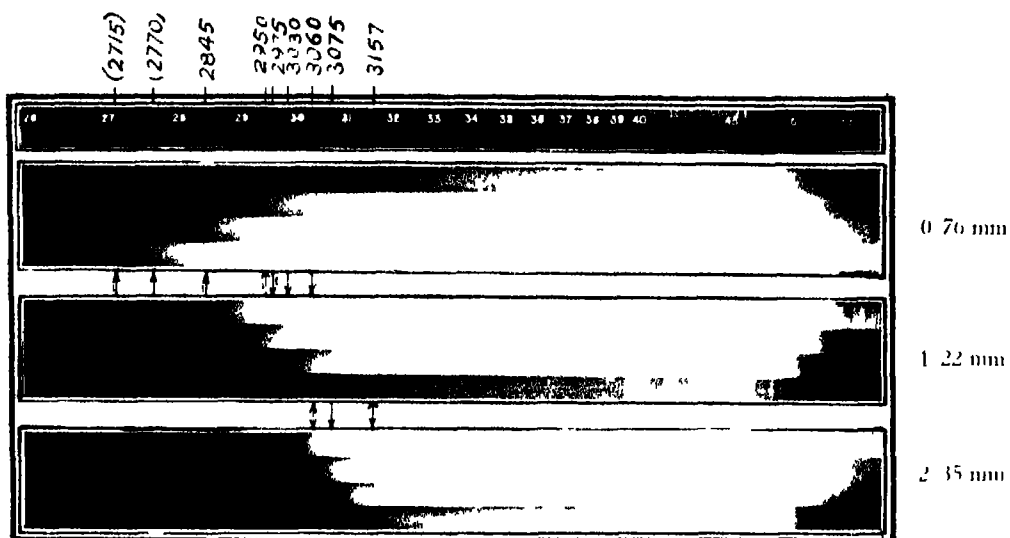


Fig. 1 Transmission ultraviolet

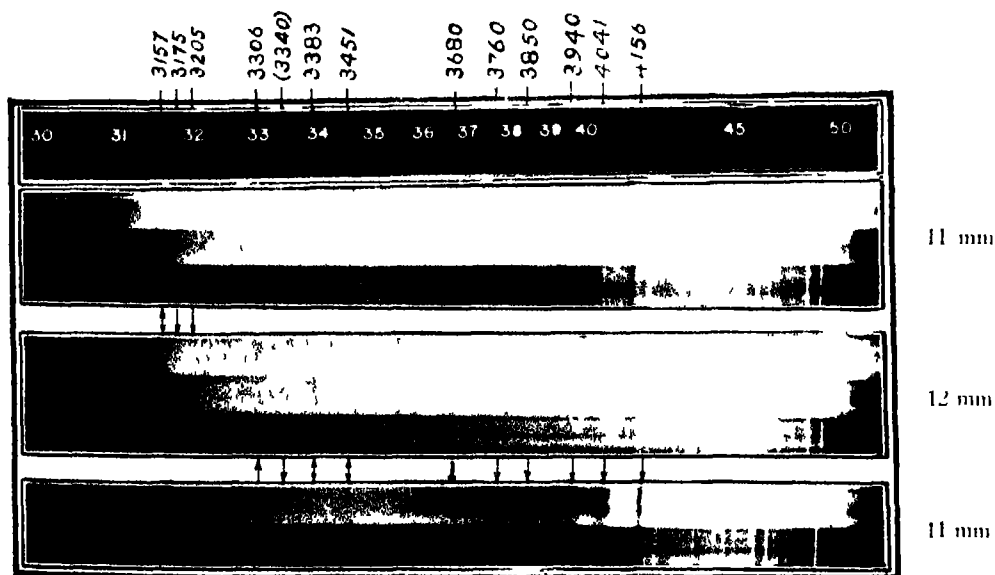
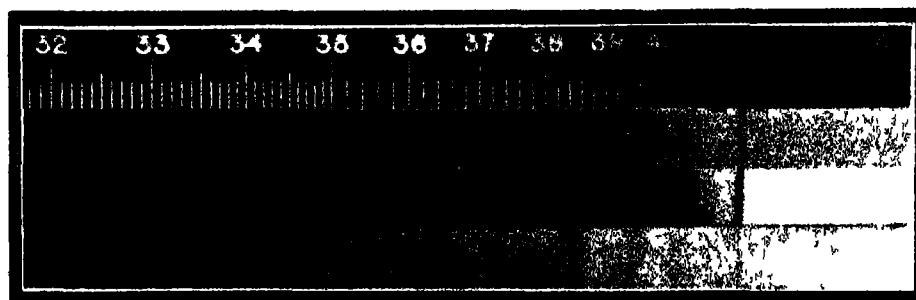
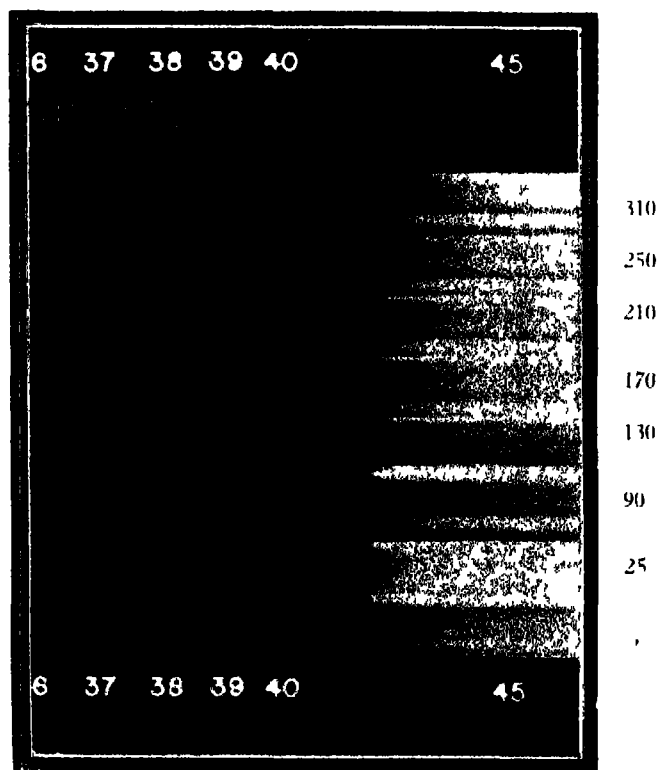


Fig. 2 Absorption bands



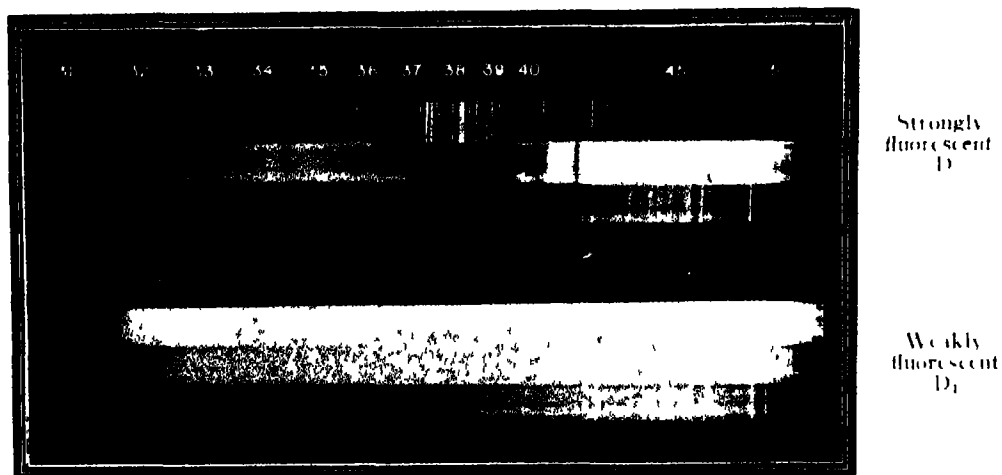
Effect of low temperature on absorption

Fig. 3



Effect of high temperature

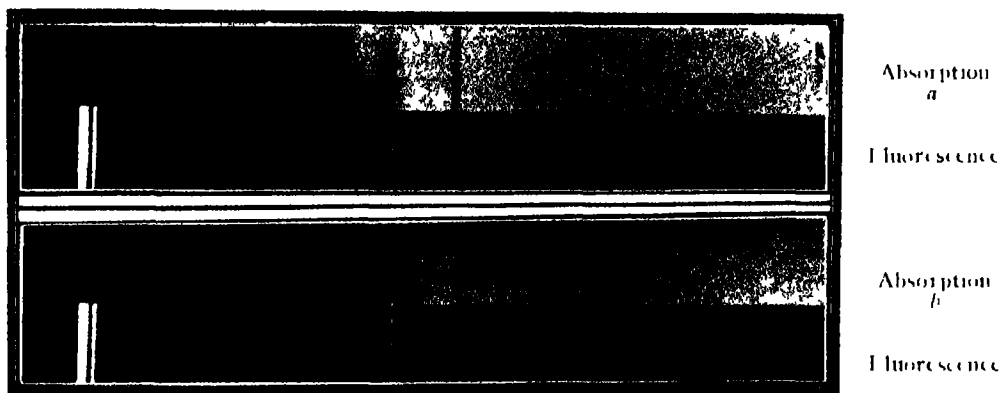
Fig. 4



Absorption in relation to intensity of fluorescence

Fig. 5

↓



Juxtaposition of absorption and fluorescence spectra (*a*) at 25° and (*b*) at 180°

Fig. 6

The diffuse band system was found to be directly related in intensity to fluorescence, being intense in strongly fluorescent crystals and *vice-versa*. The absorption and fluorescence frequencies coincide exactly at 4156, and the other diffuse bands are distributed with perfect mirror-image symmetry about this line, with absorption on the short wave-length side and fluorescence on the long wave-length side.

The wave-number differences of the absorption and fluorescent bands from 4156 were found to be nearly equal in frequency to the weak infra-red absorptions known to be exhibited by diamonds.

The symmetrical pattern of absorption and fluorescence is explained by considering 4156 as the principal electronic transition of the active centre in diamond luminescence, and the diffuse band system as arising out of combinations with lattice vibration frequencies. The absence of overlapping of emission and absorption spectra except at 4156 is explained as due to the fact that higher vibrational energies are instantaneously taken up by the entire lattice.

The probable origin of the sharp band at 4156 is discussed with reference to possible impurities and it is suggested on the basis of the available evidence that local imperfections of the lattice are responsible for the active centres.

The features of the absorption in diamond observed by the author and earlier workers are shown to be inconsistent with the electronic energy levels obtained from the theoretical calculations of Kimball. This is pointed out as showing that crystals do not actually conform to the ideal lattice, and that a certain secondary structure brings about new intermediate levels.

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THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part VII The Condensation of Piperonal

BY KANTILAL C PANDYA AND P GEORGE VARGHESE

(Chemistry Laboratory, St John's College, Agra)

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THE condensations of several aromatic aldehydes with about five of the common acid amides have already been reported with certain peculiarities of each. Thus the condensations of salicylaldehyde (Sodhi¹) showed the great effect of a trace of pyridine in the condensations, as not only did it give larger yields than what were obtained by other methods, but so far the yields from salicylaldehyde have been the highest produced from any other aldehyde, being often almost quantitative. The condensations of *m*-hydroxy-benzaldehyde (Mehra²) with the same amides present a sharp contrast, as the organic base did not materially increase—it even caused some resin-formation—and the yields were uniformly poor and were actually nil with formamide and acetamide. In the case of *p*-hydroxy-benzaldehyde (Manzur³), the yields again increased, being very nearly as good as those obtained from salicylaldehyde, pyridine again playing some part, though not as great, in increasing the yields. All the products from these three sources were, however, quite similar, chemically and physically. Physically they looked like 'organic glass', did not always give a good melting-point, though they analysed well, had a very limited solubility in the ordinary organic solvents and were more or less coloured. Chemically they were all of the benzylidene-mono-amide type, instantly decolorising Baeyer's reagent and bromine in solution, and giving characteristic colorations with concentrated sulphuric, and, often, with concentrated hydrochloric acid.

When next the methyl ethers of the three aldehydes were submitted to condensations with the same amides, there was a considerable difference, both in the nature and in the quantity of the condensation-products. Formamide did not condense with any of the three, and the other amides gave in all cases products that were saturated, that were of the benzylidene-*bis*-amide type, which crystallised and melted well, and the yields of which were either unaffected or unfavourably affected, by the presence of an organic base. The yields, though not bad, never exceeded 60% of theory (Mehra⁴).

It became a matter of interest to find out how piperonal would behave, because it is also a derivative of a dehydroxy-aldehyde, but with the two hydroxy groups replaced by one methylene-dioxy group instead of the two methoxy groups

The condensations of piperonal with amides have not been met with in literature, and in this paper are presented the results of the condensations of piperonal with eight different amides. The products obtained are in a line with those obtained from the three methoxy-benzaldehydes, *i.e.*, they are all of the benzylidene-*bis*-amide type, all well-crystallisable high-melting substances, almost all colourless, and came out best when piperonal and the amide were heated ~~alone~~, without pyridine. Here also formamide did not condense, though a variety of different conditions were tried. The yields were on the whole good: the lowest was 38% (with propionamide) and the highest 77% (with heptamide).

In the first condensation, different conditions have been tried, while in the case of the succeeding ones only the more promising conditions have been applied.

On the whole the aldehyde-amide condensations offer certain interesting but obvious contrasts in results as well as in the influence of the substituent groups with the aldehyde-malonic acid condensations that have been already reported in several parts ⁵

Experimental

Condensation with Benzamide—

(i) *Without any Condensing Agent* —(i) 1.5 g piperonal pure and 1.21 g. benzamide (1/100th mol each) were taken in a round-bottomed flask of about 50 c.c. capacity, well mixed and heated on the water-bath for three hours without a condenser. The whole mass melted to a chocolate-coloured liquid and some water-vapours were given out. It was then allowed to cool overnight, the solid mass was washed next morning with alcohol to remove the unreacted aldehyde and amide, and the white residue left was found to melt at 214° C. to a brownish liquid. This melting-point, which was so much higher than that of the amide or of the aldehyde, indicated that it was a condensation-product. On recrystallisation from alcohol, the m.p. rose to 221°. The yield was poor.

(ii) The same experiment was repeated but the heating was continued a little longer (five hours), the crude product melted at 215° and the yield was 1.4 g. The product had solidified during the heating.

(iii) The heating temperature was now 110–20° (oil-bath) The crude product was much cleaner, melted at 220°, melted after recrystallisation at 222°, and weighed 1.5 g

(iv) The oil-bath temperature was kept at 130–40° C., but this made the product reddish, gave a lower melting-point 216° (crude) and decreased the yield to 1.2 g

(v) The molecular proportions were now 1.2 mol, i.e., 1.5 g of the aldehyde and 2.42 g of the amide were used The heating at water-bath temperature was continued for five hours The yield was poor, only 1.1 g Much of the benzamide remained unacted

(vi) The same quantities were heated on the oil-bath at 125–30° for six hours, and the yield increased to 2.4 g, which is 64.17% of the theoretical. This was the best yield obtained

(ii) *In the Presence of Various Condensing Agents*—1.5 g of piperonal, 1.21 g of benzamide and 0.1 cc of pyridine (1.1012 mol) were heated on the water-bath for five hours The reacting mass did not resolidify during the heating, but was found solid next morning The crude product was very impure (m.p. 203°) and the yield only 0.4 g

When fused sodium acetate was tried (according to the method of Cebrian,^{6,7} and Titherley and Marples) in 1:1:1 mol proportions, under the same conditions as above, the product was very much coloured, melted (crude) at 205°, (purified) at 221°, but weighed only 0.1 g

Acetic acid was tried as the condensing agent (according to the method of Noyes⁸), the substances being in the proportion of 1:1:0.2 mol, the heating being for five hours on water-bath The yield was 0.8 g

The condensation-product after purification came out as colourless micro-crystals, needle-shaped, and melting at 222° It was also soluble in acetone from which it could also be crystallised, though alcohol is a much more suitable solvent It is only slightly soluble in the ordinary organic solvents like benzene, ether and chloroform. It did not decolorise Baeyer's reagent nor bromine in chloroform It gave a yellow coloration with concentrated sulphuric acid, which on a gradual addition of water produced a violet ring, and the whole solution became deep brown on shaking.

Nitrogen, found 7.34%, 7.48%, piperonyl-bis-benzamide, $C_{22}H_{18}O_4N_2$, requires 7.48% the corresponding monoamide requires 5.53%

About 1 g of the bisamide and about 15 cc of 2 N sulphuric acid were refluxed in a flask for about one hour. The solution was filtered hot

and gave on cooling, crystals of benzamide, identified by the melting-point. Piperonal was identifiable by its characteristic fragrant smell.

Condensation with Acetamide—

3 g piperonal and 2.4 g acetamide (1.2 mol) were heated as usual on a water-bath for five hours. The reacting mass melted to a chocolate-coloured liquid but solidified to a cake after 3.5 hours' heating. The usual treatment gave a white crystalline product m.p. 229° (crude), 235° (recrystallised). The yield was poor.

The same experiment was repeated at 120° (oil-bath), and produced an yield of 0.8 g.

As a good deal of acetamide had sublimed away during these two experiments, in the third experiment an air-condenser was attached to the flask in which the two were being heated, and the heating was carried on for six hours at 120–25° (oil-bath). The crude product melted at 234° yield 2.1 g or 42% of theory.

When, in another experiment, the heating was for only 30 minutes and by means of a low free flame, the reacting mass resinified and was mixed with a lot of tarry matter, from which nothing useful could be extracted. Higher temperatures are clearly detrimental.

The product crystallised out from hot alcohol in white long silky needles, melting at 237–38°. It was more soluble in hot alcohol than the corresponding benzamide condensation-product. All the other properties of this were identical with those of the latter, only with strong sulphuric acid it gave a deep colour after some time, and on the addition of water, it gave a violet ring which changed to a violet solution on shaking.

Nitrogen found 11.17%, piperonyl-*bis*-acetamide $C_{12}H_{14}O_4N_2$ requires 11.20%. the mono-compound requires 7.33%.

Condensation with Propionamide—

1.5 g piperonal and 0.73 g of propionamide (1.1 mol) were heated on water-bath as before for four hours. The mixture first melted and then set to a hard mass. The white product taken out of it as usual melted at 223°. The yield was very poor.

The reacting proportions were then changed to 1.2 mol. 1.5 g piperonal and 1.46 g propionamide were heated on a water-bath for ten hours. The product weighed 1.0 g, melting at 225° (recrystallised from hot alcohol).

The same amounts as in the second experiment were heated at 120–25° (oil-bath), but the product taken out weighed 1.0 g. only. This was the highest yield, equal to 36% of theory.

In another experiment the same amounts were heated in the same way, but for 10 hours the yield did not improve, as it was 0.9 g. Its colour also was an indication of impurity.

The product was easier to recrystallise from hot alcohol than the two earlier products: white silky needles, m.p. 225°. Its other properties were similar to those of the two preceding compounds: only with strong sulphuric acid it gave a pale yellow colour which changed to green on standing. On the addition of water, the usual violet ring was formed at the inter-surface of the two liquids, but this on shaking coloured the whole solution violet, and then immediately black.

Nitrogen, found 10.12%; piperonyl-*bis*-propionamide $C_{14}H_{18}O_4N_2$ requires 10.07%; the mono-amide requires 6.83%.

Condensation with Formamide—

(i) 3.0 g. piperonal and 1.8 g. formamide (1.2 mol) were heated in a flask fitted with an air-condenser for five hours over a water-bath. The mixture remained in the liquid condition all through. At the end, it was cooled and added to a large quantity of water, when only piperonal separated out.

(ii) The same quantities were taken, but the heating was done for ten hours on an oil-bath at 130°. The mixture remained a liquid, and when a test portion was taken out and poured into water, only piperonal was obtained. The remaining portion was then heated again for another five hours at 150°. The mass had however resinified and nothing could be separated from it.

(iii) 1.5 g. piperonal, 0.9 g. formamide and 0.1 c.c. pyridine (1.2/0.12 mol) were heated together at 130° for five hours. At the end, most of the piperonal was recovered when the mixture was poured into water.

It was evident that neither temperature nor pyridine induced the condensation in this case.

Condensation with Phenylacetamide—

(i) 1.5 g. piperonal and 2.7 g. phenylacetamide were heated together for five hours on a water-bath (1.2 moles). After about two hours the molten mass set to a hard mass. Washed with alcohol at the end, the yield was poor, the crude product melted at 219°, and the purified one at 234°.

(ii) The heating was done at 120–25° in an oil-bath for five hours. The crude product melted at 220° and weighed 2.0 g (about 50% yield).

(iii) The temperature was now 125–30°, all other conditions being the same as in (ii). The product weighed 2.2 g or 54.7% yield, and melted at 220°.

When taken out from hot alcohol, piperonyl-*bis*-phenylacetamide came out in very small colourless needles, melting at 224°. It was less soluble in the organic solvents than the products obtained from acetamide and propionamide; it was very little soluble in benzene, ether, etc.

It had no effect on Baeyer's reagent or on bromine in carbon tetrachloride. It gave a yellow colour with concentrated sulphuric acid, which deepened on standing and changed to brown on the addition of water; a violet ring was formed at the interface of the two liquids, while the solution became deep brown when shaken.

Nitrogen, found = 7.19%; piperonyl-*bis*-phenylacetamide $C_{24}H_{22}O_4N_2$ requires 6.97%, the mono-formula would require 5.24%.

Condensation with Cinnamamide—

The cinnamamide (prepared in the laboratory from cinnamic acid, and melting at 147°) 2.94 g and piperonal 1.5 g (1.2 mol) were heated together at 120° (oil-bath) for six hours. The product was extracted with alcohol. The crude piperonyl-*bis*-cinnamamide melted at 238°. When crystallised several times from alcohol, and then three times from pyridine it melted finally at 248°. It weighed 3.5 g, i.e., was 81.9% of theory. The white silky needles gave a deep yellow colouration with concentrated sulphuric acid.

Nitrogen, found = 6.65%, the *bis*-cinnamamide $C_{26}H_{22}O_4N_2$ requires 6.57%.

Condensation with n-Butyramide—

1.5 g piperonal was heated with 1.74 g *n*-butyramide in an oil-bath at 115–20° for seven hours. The reacting mass had solidified after about 3.5 hours and the heating was stopped after another 3.5 hours. The product taken out in the usual way came out in white needle crystals (hot alcohol) melting at 208°. Yield = 1.7 g or 55.6% of the theoretical. It also gave a yellow coloration with strong sulphuric acid.

Nitrogen, found = 9.40%; the piperonyl-*bis*-butyramide $C_{18}H_{22}O_4N_2$ requires 9.15%.

Condensation with n-Heptamide—

0.75 g. piperonal and 1.29 g *n*-heptamide (1.2 mol) were heated at 115–20° for seven hours. The mass which was liquid for three hours set in to a solid afterwards. The product, long white crystals (hot alcohol) melted at 163° and weighed 1.5 g. The yield was thus = 76.9% of theory.

Nitrogen, found . 7.67% the piperonyl-*bis*-heptamide requires 7.18%.

Summary

Piperonal condenses best when heated without any other condensing reagent, with seven of the common amides, giving characteristic piperonyl-*bis*amides. It does not condense with formamide.

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THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part VIII. The Condensations of 6-Nitropiperonal

BY KANTILAL C. PANDYA AND P. GEORGE VARGHESE

(Chemistry Laboratory, St. John's College, Agra)

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IN Part VII of the series have been described the condensations of piperonal with eight of the common acid amides, of which one formamide did not undergo condensation¹. Wondering whether the introduction of any active group on the ring of the aromatic aldehyde would have any observable influence on the condensations of piperonal with these amides, simple derivatives of piperonal with an active substituent were considered desirable for a trial. Two of these are available and very easily prepared from the aldehyde itself, viz., 6-nitro-piperonal and 6-bromopiperonal. In the present paper are described the experiments made to bring about the condensations of these eight amides with 6-nitropiperonal.

As in the case of unsubstituted piperonal,¹ nitropiperonal is found not to undergo any condensation with formamide, the simplest, and perhaps the most extraordinary, of the amides. Unexpectedly, the yields with propionamide, benzamide and phenylacetamide are poor, while the yields with the remaining amides are above 50%, the highest being with cinnamamide, which is found to be 83% of theory, which is indeed higher than any yield obtained also from piperonal and any of the amides. Chemically the products are of the same type, viz., the 6-nitro-piperonyl-bisamide, and share the properties of the piperonal-analogues already described. Pyridine or any other organic base was not used.

Experimental

Preparation of 6-Nitropiperonal —The following was found to be the best method of preparing it and gave nearly theoretical yields. 10 g of piperonal were slowly added, in the course of 15 minutes, to 20 c.c of nitric acid (density about 1.4), and left at room temperature for another ten minutes. (It is important that during the addition the temperature should not rise above 45°.) Water was then added, when solid nitro-piperonal came out in yellow crystals. Though described as 'colourless needles from water',

the substance is really very susceptible to the influence of light, and becomes yellow, as observed by Fittig and Remsen² Indeed the description of F M Perkins³ is more true, as the compound changes from "pale yellow to intense, most brilliant yellow on the surface" m p 95°

Attempted Condensation with Formamide—The 6-nitropiperonal, 1.0 g was mixed with 2 g of formamide (1.2 mol) and the mixture kept on a water-bath at 110–15° for 24 hours. Even then no solid separated and the whole mass remained liquid. On the addition of water, the aldehyde came out unchanged.

Condensation with Acetamide—1.95 g aldehyde and 1.2 g acetamide were heated on an oil-bath at 110–15° for six hours. After two hours a solid began to set in. The product was taken out in the usual way and crystallised from alcohol-pyridine mixture as very pale yellow needles, melting at 235°. Yield 1.8 g or 61% of theory. With concentrated sulphuric acid it gave a yellow coloration, which was changed to pale yellow on the addition of water.

Nitrogen, found 14.30% the 6-nitropiperonyl-*bis*acetamide $C_{12}H_{13}O_6N_3$ requires 14.24%

Condensation with Propionamide—3 g aldehyde and 2.2 g propionamide (1.2 mol) were heated at 110–15°. After six hours even the reacting mass remained liquid, showing that the condensation was taking place very slowly or not at all. Heating was continued for 18 hours when the mass solidified. The product was treated as usual, and after repeated crystallisations the melting-point rose to 212° and the substance came out as pale yellow micro-crystals. The yield was about 15%. With concentrated sulphuric acid it gave a yellow coloration, which became faint on the addition of water.

Nitrogen, found 12.96% the 6-nitropiperonyl-*bis*propionamide $C_{14}H_{17}O_6N_3$ requires 13.00%

Condensation with n-Butyramide—1.95 g the aldehyde and 1.74 g *n*-butyramide were heated at 110–15° for 10 hours. The product was washed with ether to remove the unreacted aldehyde and then it melted at 190°. Recrystallised from alcohol, it came out in pale buff-coloured micro-needles, melting with decomposition at 209°. With concentrated sulphuric acid it gave a yellow coloration, but when water was added a little turbidity was seen and a fine violet ring formed at the surface of the mixture on shaking and thoroughly mixing, both disappeared, leaving only a very pale yellow coloration. The yield was 2 g, or 57% of theory.

Nitrogen, found 12·33% the 6-nitro-piperonyl-*bis*-*n*-butyramide $C_{16}H_{21}O_6N_3$ requires 11·96%

Condensation with n-Heptamide—0·98 g of the nitropiperonal and 1·29 g of *n*-heptamide (1·2 mol) were heated at 110–15° for 10 hours. The mixture remained liquid for nearly six hours, after which solidifications set in. The product was washed with alcohol, and in the crude condition was brown in colour. Recrystallised from hot alcohol, it came out in pale lemon-coloured needles, melting at 185°. The yield was 1·2 g or 55% of theory. It gave a reddish yellow coloration with concentrated sulphuric acid, which on the addition of water became turbid with a violet-coloured ring; all this disappeared on shaking when only a yellow coloured solution remained.

Nitrogen, found 9·80% the nitropiperonyl-*bis*-heptamide $C_{22}H_{23}O_6N_3$ requires 9·65%

Condensation with Benzamide—0·98 g of the aldehyde and 1·31 g benzamide (1·2 mol) were heated at 110–15°; after three hours the mass became solid, and the heating was continued for another three hours. The product was then taken out, well washed with alcohol and the *bis*amide crystallized from pyridine from which it came out in pale yellow needles, melting at 248°. The yield was only about 25% of theory. Higher temperatures for the condensation were tried, but they produced resinous substances. With concentrated sulphuric acid, it gave an orange coloration, which deepened on keeping, but which, on the addition of water, changed to a pale yellow as usual.

Nitrogen found = 10·46% the nitropiperonyl-*bis*-benzamide $C_{22}H_{17}O_6N_3$ requires 10·02%

Condensation with Phenylacetamide—1·95 g of the aldehyde and 2·7 g of phenylacetamide were heated together at 110–15° for six hours. The yield was poor about 10%. The product, crystallized from pyridine, was very pale yellow, in fine needles, and melted at 231°. With concentrated sulphuric acid it gave an orange-yellow coloration, which became yellow when water was added.

Nitrogen found = 9·8% nitropiperonyl-*bis*-phenylacetamide $C_{24}H_{21}O_6N_3$ requires 9·4%

Condensation with Cinnamamide—2·0 g nitropiperonal and 3·0 g cinnamamide (1·2 mol) were heated for six hours at 110–15°. The condensation was quicker than before, and the yield 3·9 g or 82·7% of theory was the best so far obtained. Crystallised from pyridine, the product, which was pale

yellow needles, melted at 232° With strong sulphuric acid it gave a very rich orange coloration, which changed into deep yellow, when water was added

Nitrogen found = 9.32% nitropiperonyl-*bis*-cinnamamide $C_{26}H_{21}O_6N_3$ requires 9.92%

Summary

The condensations of 6-nitropiperonal with amides have been studied. The products are in their properties in a line with the products obtained from piperonal itself. In the case of acetamide and cinnamamide the yields were distinctly higher than they were with piperonal. In other cases the reaction was distinctly slower and gave lesser yields.

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CONSTITUTION OF BUTRIN

BY P SURYAPRAKASA RAO AND T R SESHADRI

(From the Department of Chemistry, Andhra University, Waltair)

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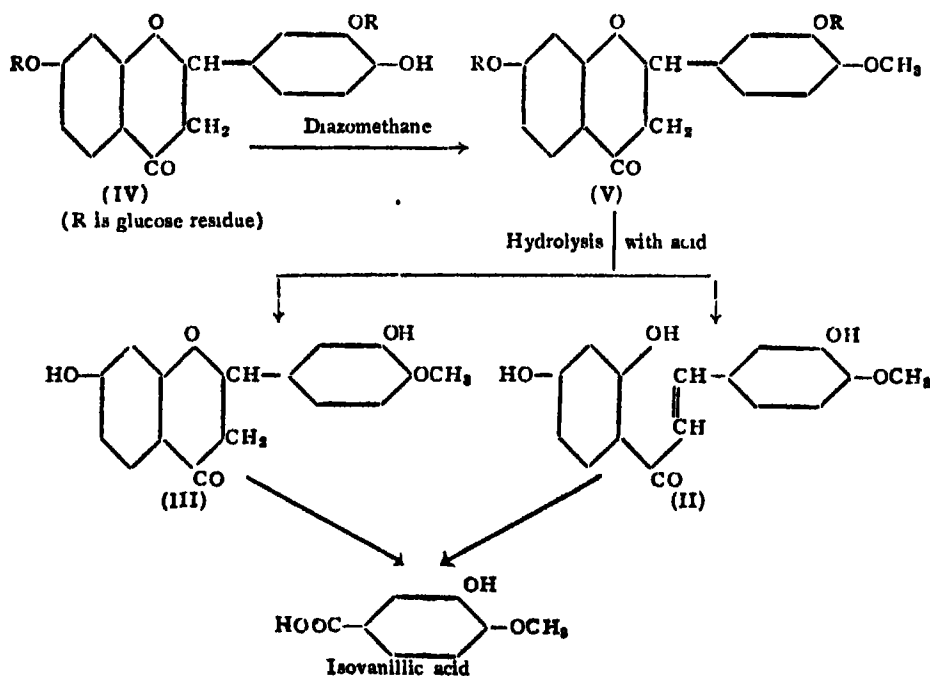
BUTRIN which was isolated by Lal and Dutt¹ from the flowers of *Butea frondosa* exhibits exceptional properties. Unlike the other flavanone glycosides, it contains no rhamnose unit and is remarkable for its sparing solubility in organic solvents and considerable solubility in water. In aqueous or alcoholic solution it gives no colour with ferric chloride. Its constitution is, therefore, of special interest in connection with the work on glycosides which is in progress in these laboratories.

The formula of butrin, $C_{27}H_{32}O_{15}$, indicates that it is a diglucoside and this has been confirmed recently by the estimation of the glucose and the aglucone obtained by acid hydrolysis.² In an attempt to establish the constitution of butrin, Lal³ subjected the glucoside suspended in ethyl alcohol to ethylation with excess of ethyl iodide and potassium carbonate. He claimed to have isolated a colourless O-diethylbutrin and an isomeric bright yellow product, and therefore concluded that butrin was a bioside, the sugar group occupying only one hydroxyl group of butin.

For the present investigation diazomethane was chosen for the methylation of the glucoside since (a) it would not open up the pyranone ring because of its mild nature and (b) there is no hydroxyl group in position 5 to offer resistance to methylation by this reagent. The reaction was carried out in aqueous methyl alcoholic solution of the substance, and the product was found to be a monomethyl butrin. When reduced with magnesium and concentrated hydrochloric acid, it gave a bright pink colour, indicating the presence of the flavanone structure. Further it was not soluble in dilute alkali, thereby showing the absence of any free phenolic hydroxyl group. By the hydrolysis of the methylated glucoside with dilute acid in order to remove the sugar residues, an extraordinary result was obtained. The resulting methyl ether (I) gave no prominent colour when treated with magnesium and hydrochloric acid, and with ferric chloride produced a marked olive brown, characteristic of butein. It was, therefore, concluded that during hydrolysis complete rupture of the pyranone ring had taken place.⁴ With a view to identify the monomethyl ether thus obtained, it was subjected to oxidative degradation with alkali and thereby isovanillic acid was produced. It should, therefore, be 4'-O-methylbutein.

In order to establish its identity further, a sample of 4'-O-methylbutrin (II) was synthesised by condensing resacetophenone and isovanillin in the presence of alkali. Though the sample (I) obtained by the hydrolysis of the methylated butrin agreed closely in its properties with the synthetic 4'-O-methylbutrin (II), it melted lower. This discrepancy which first offered great difficulties in the interpretation of the results became explicable, when it was realised later during a subsequent repetition of the experiment that (I) contained small quantities of a more easily soluble fraction (III) which differed from the major part in (a) giving no colour with ferric chloride and (b) producing a pink colour when treated with magnesium and hydrochloric acid. (III) was, therefore, a flavanone derivative. It was identified as 4'-O-methylbutrin by taking the mixed melting point with an authentic sample obtained by heating the synthetic 4'-O-methylbutrin (II) with dilute sulphuric acid for a number of hours. After the removal of this fraction, sample (I) melted correctly at $206-08^{\circ}$ and the mixed melting point with (II) was undepressed.

From the above results the conclusion is inevitable that butrin is a dimonoside of butin, bearing the two glucose units in 3' and 7 positions (IV). This explains the non-production of any colour by the glucoside with ferric chloride, the formation of only a monomethyl derivative (V) on methylating



the substance with diazomethane and the production of the monomethyl ethers of butin and butein and of isovanillic acid by degradation

It may be interesting to note here that during the course of this methylation no methyl groups entered the sugar nuclei, as had been found to take place in some other cases. Further the hydrolysis of the methylated glucoside with acids has led to the formation of the butein compound in much larger proportion than has been found with butrin itself ²

The most important outcome of the present investigation is (1) that butrin is the first instance of an anthoxanthin containing two sugar groups in two different positions, though such cases are very common in anthocyanins and (2) that it is the first example for the occurrence of a glucose unit in the side phenyl nucleus in both anthoxanthins and anthocyanins. Another case wherein the side phenyl nucleus carries the sugar residue has also been recently discovered by us (unpublished work), thus showing that such type of glucosides is more common than originally imagined

Experimental

The dried flowers of *Butea frondosa* were coarsely powdered and extracted in batches with methylated spirit. The total alcoholic extract was then distilled to recover the solvent and the concentrate was filtered, while still hot, through a fluted filter to remove the wax and the resin that separated out and then left for a week. At the end of this period, a crystalline solid along with some brown resin and wax was deposited. The contents were filtered and the residue washed with methylated spirit till it became lemon-yellow in colour. This crude product readily dissolved in boiling methyl alcohol, and when the solution was allowed to stand overnight, a pale yellow crystalline solid separated out. It was filtered and subsequently boiled with excess of methyl alcohol. This time, however, very little of the solid went into solution, as it was almost pure. It was once more boiled with excess of fresh methyl alcohol to completely remove the impurities and filtered. The substance was obtained by this procedure as almost colourless needles melting at 193–94° (decomp). It was soluble in water and the aqueous solution did not develop any colour when treated with a drop of ferric chloride. A small part was dissolved in water, excess of concentrated hydrochloric acid added and then treated with magnesium powder, when a beautiful pink colour was produced.

Preparation of 4'-O-methylbutrin—

Butrin (3 g) was dissolved in 80% methyl alcohol (200 c c) and treated with a large excess (10 g) of diazomethane in ethereal solution in small

quantities The contents were shaken vigorously after each addition. As soon as diazomethane was added, the solution became cherry red and the evolution of a small amount of gas also took place Even during the course of the addition, a colourless crystalline solid began to separate out The contents were left overnight to enable the reaction to be completed The ether and the excess of diazomethane were then expelled from the reaction products and the colourless crystalline solid filtered It was very sparingly soluble in methyl and ethyl alcohols, moderately soluble in glacial acetic acid and freely in boiling water or dilute acetic acid From dilute acetic acid solution, it crystallised as colourless needles melting at $230-32^{\circ}$ It was not soluble in cold aqueous alkali and did not give any colour with ferric chloride When reduced with magnesium powder and hydrochloric acid as already described, it developed the pink colour characteristic of flavanones The yield of the pure product was 2 g (Found in the sample dried *in vacuo* at $130-40^{\circ}$ C, 54.6, H, 5.3, OCH_3 , 5.0, $\text{C}_{27}\text{H}_{31}\text{O}_{14}$ OCH_3 requires C, 55.1, H, 5.6, OCH_3 5.1%)

Hydrolysis of Methylbutrin—

Experiment 1—Methylbutrin (0.5 g) was treated with 7% sulphuric acid (25 c.c.) and the mixture boiled under reflux on a wire-gauze The solid went into complete solution within 5 minutes and after about 45 minutes, some yellow solid separated out giving rise to bumping However, the heating was continued for 2 hours to complete the hydrolysis The contents were then cooled and filtered The residue was purified by crystallisation from dilute acetic acid It was deep yellow in colour and produced an olive brown colour when treated with ferric chloride in dilute alcoholic solution When reduced with magnesium and concentrated hydrochloric acid, it did not give the brilliant pink colour characteristic of flavanones (Found OCH_3 , 11.2, $\text{C}_{18}\text{H}_{11}\text{O}_4$ OCH_3 requires OCH_3 , 10.8%) The substance melted at $196-98^{\circ}$

Oxidative Degradation of the Above Product. Isolation of Isovanillic Acid—

The substance (0.5 g) was treated with 50% potash (20 c.c.) in a silver flask and heated under reflux for 6 hours At the end of the period, the clear alkaline solution was acidified with hydrochloric acid and extracted with ether From the ether solution an acid melting at $253-55^{\circ}$ was obtained It was found to be identical with isovanillic acid

Experiment 2—(a) *Preparation of 4'-O-methylbutein.* The hydrolysis of the methylated glucoside was carried out as already described After the heating was over, the contents were immediately filtered hot and the filtrate allowed to cool The residue was crystallised from dilute alcohol and was

obtained as deep yellow microcrystalline powder melting at 206–08°. It was sparingly soluble in water but it dissolved freely in alcohol or acetic acid. When treated with a drop of ferric chloride, an aqueous alcoholic solution of the substance gave an olive brown colour. On reduction with magnesium and hydrochloric acid the substance did not develop any pink colour. It was found to be identical with a synthetic sample of 4'-O-methylbutein and admixture with it did not depress the melting point (Found OCH_3 , 11.0, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{OCH}_3$ requires OCH_3 , 10.8%)

(b) *Preparation of 4'-O-methylbutin*—The hot aqueous filtrate left after the separation of the methyl butein deposited on cooling a pale yellow substance. It was filtered and recrystallised from dilute alcohol, when it came out as pale yellow glistening rectangular plates melting at 204–06°. In alcoholic solution it did not yield any colour with ferric chloride, but on reduction with magnesium and hydrochloric acid it gave a beautiful pink colour. It was identical with a synthetic sample of 4'-O-methylbutin, and the mixed melting point with it was undepressed (Found OCH_3 , 11.1%, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{OCH}_3$ requires OCH_3 , 10.8%)

This compound could be easily distinguished from the isomeric 4'-O-methylbutein, since it was only pale yellow in colour and crystallised as glistening rectangular plates, whereas the butein ether was a deep yellow microcrystalline powder. The melting point of a mixture of the two substances was 188–91°

Synthesis of 4'-O-methylbutein—

The conditions for the preparation of chalkones according to the method of Kostanecki have recently been studied in these laboratories⁵, and it has been found that the best yields could be obtained by (1) taking an excess of one of the components (aldehyde or ketone) the choice being dependent on the availability of the particular substance and (2) refluxing immediately after the addition of the alkali to the reactants for an hour. This procedure was adopted in the synthesis of 4'-O-methylbutein.

Isovanillin (1 g, 1 molecular proportion) and resacetophenone (3 g, 3 molecular proportions) were dissolved in 10 c.c. of alcohol and 25 c.c. of 50% potash were added to the solution at the room temperature. The mixture was refluxed for one hour on a water-bath and then kept out of contact with air for 24 hours. The product was then diluted and acidified with hydrochloric acid, cooling the flask under the tap. A yellow product separated out. It was filtered and recrystallised from alcohol. It came out as a microcrystalline powder melting at 206–08°. The yield of the pure product was 1 g. (Found C, 65.2, H, 5.6, OCH_3 , 10.6; loss on drying *in vacuo*

at 120–30°, 2.8, $C_{15}H_{11}O_4 \cdot OCH_3 \cdot \frac{1}{2}H_2O$ requires C, 65.1; H, 5.4, OCH_3 , 10.5, loss on drying (H_2O), 3.1%

Synthesis of 4'-O-methylbutin —

The above methylbutein (1.5 g) was dissolved in 50% alcohol (75 c.c) and treated with concentrated sulphuric acid (3 c.c). The solution was then boiled under reflux on a water-bath for 18 hours. It was then diluted with boiling water to 250 c.c when a solid began to separate out. On shaking and slight cooling the solid coagulated. It was filtered and recrystallised from alcohol. It was a deep yellow substance melting at 205–07° and was found to be identical with the starting material. The filtrate deposited some more solid on cooling. It was only pale yellow in colour and crystallised from dilute alcohol as glistening rectangular plates. It produced the pink colour characteristic of flavanones, when reduced with magnesium and hydrochloric acid. It melted at 203–05°. Yield of the pure product was 0.5 g. (Found C, 67.0, H, 4.9; OCH_3 , 11.0, $C_{15}H_{11}O_4 \cdot OCH_3$ requires C, 67.1, H, 5.1; OCH_3 , 10.8%.)

Our thanks are due to Mr G. V. L. Narasimha Murthy for some of the microanalyses.

Summary

On treatment with diazomethane, butrin gives rise to a monomethyl ether which yields on hydrolysis with acids a mixture of 4'-O-methylbutin and 4'-O-methylbutein, the latter being the major component. The constitutions of these two products have been established by alkaline oxidation, yielding isovanillic acid and comparison with synthetic samples. It is, therefore, concluded that butrin is 3'-7-diglucoside of butin, and thus it is the first instance of a glycoside to contain the sugar residues in two different positions amongst the group of anthoxanthins and also the first instance to carry a sugar group in the side phenyl nucleus amongst both anthoxanthin and anthocyanin pigments.

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A NOTE ON THE METHYLATION OF QUERCETAGETIN

BY P SURYAPRAKASA RAO

(*Department of Chemistry, Andhra University, Waltair*)

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(Communicated by Prof T R Seshadri, M A , Ph D , F I C , F A S C)

THE methylation of the hexahydroxy flavone, quercetagenin with methyl iodide and potash was first carried out by Perkin¹ Though an excess of the reagents was used, the main product was the pentamethyl ether, and the completely methylated substance was obtained in very small amounts As an alternative method for the preparation of the hexamethyl ether, Perkin subjected the dry potassium salt of the pentamethyl compound to the action of dimethyl sulphate, but the yield was poor even then The pentamethyl ether (3 6 7 3' 4'-) was subsequently prepared by Baker, Nodzu and Robinson² during the course of the synthesis of quercetagenin These authors could effect further methylation of the pentamethyl ether very satisfactorily by treating the compound in acetone solution with dimethyl sulphate and alkali

It has now been found that the hexamethyl ether can be readily prepared in a very satisfactory yield (about 90%) according to the method of Rao and Seshadri³ The acetyl derivative was dissolved in acetone and the solution treated with the requisite amounts of dimethyl sulphate and 20% sodium hydroxide alternately in small amounts Finally the medium was made definitely alkaline by the addition of further quantities of the alkali After leaving overnight the acetone was removed by heating on a water-bath, and when the remaining alkaline solution was acidified, the hexamethyl ether was produced After crystallisation from alcohol using a little animal charcoal, the substance was obtained as narrow rectangular plates melting at 142-44° Mahal⁴ followed a similar method with slight alterations but the yield was recorded to be only 33% on the weight of the acetate taken

The action of diazomethane on quercetagenin does not seem to have been studied before An anhydrous methyl alcohol or dioxan solution of the flavonol was treated with excess of diazomethane in ethereal solution, adding the latter in small quantities during two days After evaporating off the solvent, a brown oily liquid was obtained, which solidified on adding a little

water and keeping in the ice-chest for some time. The brown solid was purified by crystallisation from alcohol using a little animal charcoal. Hexamethyl quercetagetin melting at 142–44° was obtained in an yield of 80%

The action of methyl iodide and anhydrous potassium carbonate has recently been studied in our laboratories on some of the flavonols, herbacetin, gossypetin and quercetin, and their action has been found to be similar to that of diazomethane⁵. A deviation has been noticed in the case of quercetagetin. When a solution of the flavonol in dry acetone was treated with anhydrous potassium carbonate, the pigment got precipitated almost completely, and the subsequent boiling of the mixture with methyl iodide for 60 hours did not bring about any methylation, the original substance being recovered unchanged. The experiment was repeated using a mixture of dioxan and dry acetone to dissolve the pigment. Even now the flavonol got precipitated on adding anhydrous potassium carbonate, but on boiling with methyl iodide a pale yellow substance began to float over the surface of the liquid. It was mechanically separated out and crystallised from alcohol, when it appeared as almost colourless rectangular plates melting at 160–61°. It was found to be identical with 3, 6, 7, 3', 4'-pentamethyl quercetagetin, developing a brown colour with a trace of ferric chloride and giving a dull olive-green with an excess. The yield too was poor.

The author's thanks are due to Prof. T. R. Seshadri for his interest in this work.

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ON GUEST'S LAW OF ELASTIC FAILURE

BY B R SETH

(From the Department of Mathematics, Hindu College, Delhi)

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VARIOUS hypotheses have been advanced for determining the yield point of an elastic material. In one group we may combine the hypotheses of (i) principal maximum stress, (ii) maximum principal strain and (iii) maximum shear stress or maximum principal stress difference. Of these the last one seems to find favour with many writers. In fact Cook¹ maintains "that stress differences alone will be found in the expression of any theory which can be applicable" to elastic failure. Taylor and Quinney² also hold this view.

A second group of theories starts from the idea that there is a limit to the amount of strain energy which can be stored in the element of volume of an elastic material. The strain energy can be split into two parts, one due to the change in volume and the other due to the distortion. Haigh³ and Beltrami³ take into consideration both these changes, but Mises⁵ and Hencky neglect the part due to the change in volume. Nadai⁶ is a great supporter of the Mises-Hencky hypothesis.

A feature common to all these theories is that the criterion of failure is unaltered by a reversal of the sign of the stress. But it is well known that materials shew yield stresses in compression several times those in tension. To avoid this objection Mohr⁷ has extended the maximum shear theory by combining it with the principal maximum stress theory.

Very few have found their way to agree to Guest's criterion⁸ that besides the shearing stress, which is a primary factor in yield, volumetric stress of a certain type should also be taken into account. In two recent papers⁹ he has elaborately discussed some recent experimental results of Mason, Becker and Cook, and has shewn how the difficulties in the explanations given by the various authors and others of their results can be overcome by taking a volumetric stress in the shearing stress hypothesis. We propose to shew how the theory of Finite Strain which has been developed in some recent papers^{10, 11} gives a criterion similar to that of Guest, which contains the three commonly adopted theories of maximum shear stress, of Mohr and of Mises and Hencky.

Let p_1, p_2, p_3 be the principal stresses in descending order of magnitude. If we adopt the maximum stress difference hypothesis, the criterion can be written as

$$p_1 - p_2 - \text{Constant} = K \text{ (say)} \quad (1)$$

In the case of a simple tension in the x -direction we can put $p_1 = \widehat{xx}$, $p_2 = 0$, so that $p_1 = \widehat{xx} = K$. In the case of pure shear we can put $p_1 = -p_2 = \widehat{xy}$, so that $\widehat{xy} = \frac{1}{2} K$. Hence, if ξ be the ratio between the yield point in tension and the yield point in shear, we get $\xi = 0.5$

Mises-Hencky hypothesis can be written as

$$(p_1 - p_2)^2 + (p_2 - p_3)^2 + (p_3 - p_1)^2 = K \text{ (a constant)} \quad (2)$$

Proceeding as above we find $\xi = 0.577$

Guest formulates the law of failure as

$$p_1 - p_3 + k(p_1 + p_3) = K \text{ (a constant)}, \quad (3)$$

where k is a non-dimensional constant of the material varying from zero to unity. For $k = 0$ (3) reduces to (1), and for $k = 0.155$ (3) gives the same value of ξ as (2). In general the value of ξ given by (3) is

$$\xi = \frac{1}{2}(1 + k) \quad (4)$$

The values of ξ determined experimentally have a wide variation, and hence (3) can be expected to give better results than either (1) or (2). It is significant that Guest does not use the average volumetric stress $\frac{1}{3}(p_1 + p_2 + p_3)$ but the stress $\frac{1}{2}(p_1 + p_3)$. In the finite strain theory it is found that $\frac{1}{3}(p_1 + p_2 + p_3)$ should be used.

For a spherical shell subjected to uniform normal tractions on the inner and outer surfaces the finite strain theory gives the limits for the principal stresses \widehat{rr} and $\widehat{\theta\theta} (= \widehat{\phi\phi})$ as¹²

$$-\frac{1-2\eta}{1+\eta} < \frac{2(\widehat{rr} - \widehat{\theta\theta})}{3k - 2\widehat{rr}} < \frac{1-2\eta}{2\eta}, \quad (5)$$

where η is Poisson's ratio and k the modulus of compression. The lower limit corresponds to infinite contraction and the upper to infinite extension.

If we take the upper limit, we get the criterion for failure due to extension as

$$\widehat{rr} - \widehat{\theta\theta} + \frac{1-2\eta}{1+\eta}(\widehat{rr} + \widehat{\theta\theta}) = 3k \frac{1-2\eta}{1+\eta}, \quad (6)$$

which is of the form proposed by Guest. For steel we can put $\eta = 0.3$ and

we get the ratio ξ equal to 0.625, which is a very high value. But, if we write (6) as

$$\widehat{rr} - \widehat{\theta\theta} + \frac{1}{2} \cdot \frac{1-2\eta}{1+\eta} (\widehat{rr} + \widehat{\theta\theta} + \widehat{\phi\phi}) = \frac{2}{3} \frac{E}{1+\eta}, \quad (7)$$

where E is Young's modulus, we get a slight modification of Guest's Law as

$$p_1 - p_3 + \frac{1}{2} \cdot \frac{1-2\eta}{1+\eta} (p_1 + p_2 + p_3) = \frac{2}{3} \frac{E}{1+\eta} \quad (8)$$

For a pure shear we can put $p_1 = -p_3 = \widehat{xy}$ (say), $p_2 = 0$, and we get

$$2 \widehat{xy} = \frac{2}{3} \frac{E}{1+\eta} \quad (9.1)$$

For a pure tension we can put $p_1 = \widehat{xx}$ (say), $p_2 = p_3 = 0$, and we get

$$\widehat{xx} = \frac{1}{3} E. \quad (9.2)$$

Hence
$$\xi = \frac{2}{3} \frac{1}{1+\eta}, \quad (9.3)$$

which lies between 0.5 and 0.75. For steel we can take $\eta = 0.3$, and the value of ξ becomes 0.577, which is exactly that given by Mises-Hencky theory.

For contraction we take the lower limit, and the criterion corresponding to (8) is found to be

$$p_1 - p_3 + \frac{1}{2} \cdot \frac{1-2\eta}{1+\eta} (p_1 + p_2 + p_3) = \frac{2}{3} \frac{E}{1+\eta}. \quad (10)$$

For a pure shear

$$2\widehat{xy} = \frac{2}{3} \cdot \frac{E}{1+\eta}, \quad (11.1)$$

and for a pure tension

$$\widehat{xx} = \frac{1}{3} \frac{E}{2-\eta} \quad (11.2)$$

The corresponding value of ξ is therefore

$$\xi = \frac{1}{2} \frac{2-\eta}{1+\eta},$$

which, as was to be expected, is equal to 0.577 for a higher value of η given by $\eta = 0.392$.

The ratio of the values of \widehat{xx} in pure compression and in tension is found from (9.2) and (11.2) as

$$\frac{3}{2-\eta},$$

which varies between $\frac{1}{2}$ and 2. Thus, as is proved by experiment, the yield stresses in compression are much greater than those in tension.

It should be mentioned that the laws formulated in (8) and (10)* are based on the hypothesis that the material remains within the limits of perfect elasticity. But Guest has shown his law to hold good for brittle materials as well. Whether we use $\frac{1}{2}(p_1 + p_2)$, as Guest has done, or the average volumetric stress, as has been done in (8) and (10), it appears certain that an extension of the maximum shear stress hypothesis lies in including some more linear terms in the principal stresses. If the additional terms are to reflect the effect of the change in volume, the inclusion of the average volumetric stress $\frac{1}{3}(p_1 + p_2 + p_3)$ seems to be more feasible than $\frac{1}{2}(p_1 + p_2)$, as has been done by Guest.

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* For a thick cylindrical tube under normal tractions on the inner and outer surfaces an equation similar to (10) can be obtained.¹³

RAMAN EFFECT IN POTASSIUM TARTRATE CRYSTAL

BY B LAKSHMAN RAO

(From the Department of Physics, Indian Institute of Science, Bangalore)

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NEDUNGADI (1940) made an exhaustive study of the Raman effect in Rochelle salt crystals. Using a commercially available large single crystal, he obtained a number of new lines including several new lattice lines and showed that the intensity of these varied with the orientation of the crystal. The available data on single tartrates are, however, incomplete. Canals and Peyrot (1938) have recorded some high frequency lines above 1200 cm^{-1} in potassium tartrate using the crystal powder technique. Gupta (1938) reported only five lines having frequency shifts 888 cm^{-1} and above and failed to record any on the low frequency side, though he used a single crystal of sodium tartrate for the study. In view of these facts, it was felt desirable to investigate single crystals of some simple tartrates. The results obtained with a fairly large single crystal of potassium tartrate prepared by the author are reported in the present communication.

The frequency shifts (in wave numbers per centimetre) observed in potassium tartrate crystal are listed in Table I along with the relevant data of previous investigators for comparison. Columns 2 and 6 of the table contain the frequency shifts deduced from the graphical representation given by Peyches (1934) in a 2 M solution of the salt.

A glance at the table shows that many new lines, including three intense low frequency lattice oscillations and one band due to water of crystallisation, have been recorded here for the first time. It is to be noted that every line observed in the solution of potassium tartrate has a corresponding line in the crystal, though the reverse is not always true. Further, there is close agreement between the frequencies observed by Nedungadi (1940) in the case of Rochelle salt and those observed in potassium tartrate by the present author. These show clearly that the frequencies characteristic of the tartrate ion are practically unchanged by the cation in these crystals. However, the differences are conspicuous in the low frequency lattice oscillations. The three lines 77, 103 and 150 correspond respectively to the lines 88, 132, and 178 in Rochelle salt, though the former set of lines have uniformly lower values. This lowering of the lattice frequencies in potassium tartrate is perhaps to be ascribed to the larger mass of the two potassium cations than that of sodium and potassium taken together in Rochelle salt molecule.

TABLE I

Raman lines in potassium tartrate			Nedungadi Rochelle Salt Single crystal	Raman lines in potassium tartrate			Nedungadi Rochelle salt Single crystal
Canals and Peyrot Crystal powder	Pyches 2 M solution	Author Single crystal		Canals and Peyrot Crystal powder	Pyches 2 M solution	Author Single crystal	
			39 (4?)				915 (0)
		77 (8)	88 (5bd)		1000	995 (2)	990 (6)
		103 (12)	132 (8s)		1070	1073 (1)	1070 (7)
		150 (6)	178 (6vb)		1110	1110 (1)	1112 (3)
			249 (3d)	1232 f	1220	1219 (1)	1210 (3)
			380 (1bd)	1271 f		1323 (4)	1292 (4)
				1337 f			
		493 (1)	485 (3d)			1351 (2)	1347 (4d)
	525	531 (2)	532 (3)		1370		1379 (7)
	600	603 (1)	611 (4d)	1424 bf	1430 1600	1425 (4b)	1425 (4d)
			641 (0)	1607 f		2926 (10)	2935 (15)
	710		699 (1)	2652 f			2979 (8)
	810	807 (4)	811 (4d)	2739 ? 2940 F			3262
	850	846 (2)	847 (5)	2992 F		3336 (2b)	3400, 3468
	900	889 (2)	891 (7)				3534

Only one line characteristic of the C-H bonding at 2926 has been recorded in the present investigation, though Canals and Peyrot report other weak lines also

The absence of the C=O frequency in the spectrum is characteristic of the ionised carboxyl group as in the case of Rochelle salt

The author is indebted to Professor Sir C V Raman, Kt, FRS, NL, for his inspiring interest and to Mr T M K Nedungadi for useful help.

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COLOUR ANALYSIS AND COLORIMETRY

Part I. Nitrate Estimation

BY G V L N MURTY

(From the Department of Chemistry, Andhra University, Waltair)

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(Communicated by Prof T R Seshadri)

IN regard to the colorimetric methods of analysis the existing literature shows that no systematic attempt has been made to specify the various colours that are met with in terms of brightness, dominant wave-length and purity, which are the parameters that correspond very closely to the three psychological attributes brilliance, hue and saturation. Further, an analysis of the colours developed at various concentrations of the substance under investigation, can yield information regarding the limits of concentration for obtaining the maximum accuracy. Of the methods that are employed in colorimetric estimations the dilution and the balancing methods depend on the applicability of Beer's law to the solutions concerned. For the success of a colorimetric estimation by these two methods, therefore, it is necessary that the dominant wave-length of the final coloured solution at various concentrations should be nearly the same and that the brightness should neither be too low nor too high. It is obvious that the errors in the matching of colours will be considerable if the solutions are too bright or too dull. Investigations have been, therefore, undertaken with a view (1) to specify the colours that are met with in some of the important colorimetric methods in terms of brightness, dominant wave-length and purity and (2) to see how far it would be possible to correlate the limits of maximum accuracy obtained in some colorimetric estimations by the dilution and the balancing methods with those that could be judged from colour analysis data. The present paper deals with the colorimetric estimation of nitrate by employing the phenol sulphonic acid¹ and the α -naphthol sulphonic acid² reagents.

Experimental

The phenol sulphonic acid reagent was prepared as described in 'Photometric Chemical Analysis'.³ The preparation of the α -naphthol sulphonic acid reagent and the treatment of the water samples for the development of colours for comparison were carried out as described by Murty and Gopala Rao.⁴ Colour analysis was effected by making use of the Keuffel and Esser colour analyser.⁵ From the percentage transmissions at the various wave-lengths the red, green and violet sensations and the relative luminosity

values were obtained by using the K & E slide rule. The colour triangle was employed for the evaluation of purity and the dominant wave-length. The colorimetric estimations were effected by making use of the Duboscq colorimeter.

Results and Discussions

The following table gives in detail the data concerning the colour analysis of the solution which contains 0.25 mg of nitrate nitrogen. The colour was developed with the α -naphthol sulphonic acid reagent.

TABLE I

Wave-length m μ	Mean colour- analyser reading	Red sensation	Green sensation	Violet sensation	Relative luminosity
490	9	0.42	1.74	2.22	0.018
500	24	2.30	7.30	3.35	0.075
510	35	6.20	16.20	3.35	0.185
520	41	11.30	25.00	2.94	0.282
530	55	20.20	38.20	2.80	0.464
540	62	27.80	45.50	2.13	0.600
550	65	33.00	48.50	1.40	0.650
560	61	34.00	42.50	0.80	0.600
570	63	38.00	39.40	0.52	0.590
580	61	37.50	30.50	0.29	0.525
590	69	43.50	24.30		0.515
600	57	33.70	13.10		0.350
610	58	30.80	7.60		0.282
620	51	21.40	3.42		0.184
630	47	14.80	1.52		0.117
640	56	11.80	0.61		0.088
650	50	6.25	0.16		0.046
660	55	3.90			0.024
670	55	2.22			0.012
680	47	1.03			0.005
690	48	0.60	..		0.004
700	50	0.60	..		0.005

From this data the usual calculations yield the following results:

Brightness	54 0%
Dominant wave-length	575 m μ
Purity	95 0%

The values given below have been obtained by the colour analysis of the corresponding solution where the phenol sulphonic acid reagent was employed

Brightness	68 5%
Dominant wave-length	570 m μ
Purity	81·0%

Nitrate solutions of varying concentrations were treated both with the phenol sulphonic acid and the α -naphthol sulphonic acid reagents and the final coloured solutions analysed. The following table embodies the values of dominant wave-length and brightness at the different concentrations of nitrate

TABLE II

Concentration (m g $\times 10^3$ nitrate nitrogen)	Colour developed with the phenol sulphonic acid reagent		Colour developed with the α - naphthol sulphonic acid reagent	
	Dominant wave-length (m μ)	Brightness (%)	Dominant wave-length (m μ)	Brightness (%)
2 5	560	90 0	573	68 0
7 5	563	80 0	574	60 2
12 5	565	75 0	574	58 3
25 0	570	68 5	575	54 0
50 0	570	62 3	578	42 0
75 0	572	61 1	580	40 3
125 0	573	60 3	582	38 0
250 0	578	59 1	590	29 0
500 0	583	59 0	599	15 0

From the above results it is clear that solutions having the same nitrate content yield colours exhibiting longer dominant wave-length with the α -naphthol sulphonic acid reagent than with the phenol sulphonic acid reagent. Further, the percentage brightness is always lower in the former case than in the latter. In other words the α -naphthol sulphonic acid reagent yields deeper colours than the phenol sulphonic acid reagent. An examination of

the results presented in Table II shows that as far as the constancy of dominant wave-length for small changes in concentration is concerned both the methods are equally satisfactory. The brightness values, however, exhibit certain interesting features. With low concentrations of nitrate the phenol sulphonic acid reagent seems to yield colours whose brightness is very high. Hence according to the criteria mentioned in the introduction, this method does not appear to be capable of being employed for the accurate analysis of samples having low concentration of nitrate nitrogen ($< 10 \text{ mg} \times 10^{-2}$ of nitrogen). The brightness values of the corresponding colours with the α -naphthol sulphonic acid reagent, however, are neither too high nor too low. Hence this reagent should be capable of being used for the accurate estimation of nitrate solutions even at these very low concentrations. The situation seems to be the reverse in the case of strong solutions of nitrate. The α -naphthol sulphonic acid reagent cannot be useful because the brightness of the solutions is too low. The phenol sulphonic acid reagent on the other hand, yields colours whose brightness is within limits and hence it could be expected to be suitable in this range of concentration. For solutions of moderate concentrations both the methods seem to be equally satisfactory. With a view to verify these ideas colorimetric estimations have been carried out with both the reagents over a wide range of concentration and the results are given below.

TABLE III

Note —The amounts of nitrate are expressed as $\text{m.g} \times 10^2$ of nitrate nitrogen

Amount of nitrate taken	Nitrate found with phenol sulphonic acid reagent	Nitrate found with α -naphthol sulphonic acid reagent
2.5	..	2.4
5.0	..	4.8
7.5	5.6	7.5
10.0	8.2	9.9
20.0	18.9	20.0
30.0	29.5	29.8
50.0	50.2	49.6
75.0	75.0	74.8
100.0	99.9	99.1
200.0	200.0	180.0
250.0	252.0	200.0
500.0	506.0	350.0

The above results clearly show that the α -naphthol sulphonic acid could be successfully employed for the estimation of nitrate even at very low concentrations where the phenol sulphonic acid reagent is not satisfactory. At higher concentrations the reverse happens to be true. Judging both from the colour analysis as well as the colorimetric data it can be concluded that for the estimation of nitrate the α -naphthol sulphonic acid and the phenol sulphonic acid methods are both complementary, each being efficient in its own range of concentration.

Summary

The analysis of colours that are met with in the colorimetric estimation of nitrate by the phenol sulphonic acid and the α -naphthol sulphonic acid reagents has been effected by means of the Keuffel and Esser colour analyser. From the results of colour analysis as well as those of colorimetric estimations it has been shown that the α -naphthol sulphonic acid method and the phenol sulphonic acid method are both complementary, each adding to the utility of the other by being efficient in its own range of concentration.

In conclusion, the author desires to thank Prof T R Seshadri for his kind interest in the work.

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RAMAN SPECTRA OF SOME CRYSTALLINE NITRATES AND SULPHATES

By B LAKSHMAN RAO

(From the Department of Physics, Indian Institute of Science, Bangalore)

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(Communicated by Sir C V Raman, Kt, FRS, NL)

1 Introduction

INVESTIGATIONS with crystalline nitrates in the form of powder have figured prominently in the early studies on the Raman effect. Krishnamurti (1930) made extensive studies on a series of nineteen nitrates, using suitable filters to avoid the continuous background in the spectrum. In certain cases he succeeded in recording the low frequency lattice lines in addition to the frequencies characterising the internal oscillations of the nitrate ion. Gerlach (1930) and I. R. Rao (1934) also investigated a few nitrates but their spectra were very incomplete. They obtained no lattice lines, and even in the case of internal oscillations only the strongest Raman lines were recorded. More recently, Anantakrishnan (1937) reinvestigated a large number of nitrates using his technique of complementary filters and noticed several fainter lines due to the internal oscillations of the NO_3 ion, which had been overlooked by the earlier workers. The advantage of using single crystals in enabling the low frequency lattice oscillations to be recorded was made evident by the work of Nisi (1933) in the case of nitrates of the alkali metals. Other nitrates do not, however, appear so far to have been investigated in the form of single crystals. The present author has prepared fairly large single crystals of strontium, barium and lead nitrates and studied their Raman spectra, revealing a series of low frequency lattice lines in each case.

Using the powder technique, Krishnamurti (1930) also studied a number of sulphates but failed to notice any of the low frequency lines and recorded only the strongest of the lines due to the internal oscillations of the SO_4 ion in most of the cases. This is not surprising in view of the fact that the sulphates scatter light rather feebly. Nisi (1931), using small single crystals obtained better results, more lines characteristic of the SO_4 ion being recorded as also the low frequency lattice lines in copper sulphate and potash alum. Nevertheless, Nisi's data were evidently incomplete. In view of this, the present author has prepared and studied the Raman spectra of fairly large

crystals of ferrous sulphate, ferrous ammonium sulphate, magnesium sulphate, zinc sulphate, manganese sulphate and potassium aluminium sulphate. As the bands due to the water of crystallisation in the above sulphates were not recorded with sufficient intensity in the spectrograms of the single crystals, they were specially studied using Anantakrishnan's technique of complementary filters.

2 Experimental

Preparation of large single crystals from solutions under thermostatic control was tried, but on account of the unsteady supply of electric current satisfactory results were not obtained. Recourse was therefore had to the method of slow evaporation. The crystallisations were carried out in an underground chamber, the temperature of which was found to be practically constant at about 27°C . A specially designed glass frame was used to hang a nuclear crystal with a fine silk fibre. A glass plate put on the frame protected the growing nucleus from parasitic crystals.

For the study of the spectra of single crystals, a Hilger two-prism spectrograph of high light gathering power, with a dispersion of about 28°A/m m in the 4358 region, was used. For the study of the water bands a Fuess glass spectrograph with a dispersion of about 20°A/m m in the 4046 region was used. Ilford selochrome plates with special backing were employed to record the spectra. The plates were measured with the aid of a Hilger cross-slide micrometer and for comparison an iron arc spectrum was recorded alongside the Raman spectrum.

Some of the sulphates exhibited marked efflorescence. This was remedied by protecting the polished faces from tarnishing by cover glasses attached with a trace of Canada balsam in xylene. They also showed slight fluorescence which could not be got rid of even after several crystallisations.

3 Results

The Raman frequencies observed by the author in the case of the nitrates and sulphates are collected in Tables I and II. The intensity maxima

TABLE I

Nitrates	Lattice Oscillations					Frequencies of the NO_3 ion				
Strontium	109 (6)	129 (1)	142 ($\frac{1}{2}$)	167 (2)	184 (6)	736 (4)	1057 (12)		1402 ($\frac{1}{2}$)	1423 ($\frac{1}{2}$)
Barium	82 (8)	134 (7)		160 (5)		728 (1)	1047 (12)	1383 (2)		
Lead	92 (10)		144 (2)	160 (4)		725 (1)	1046 (12)	1383 ($\frac{1}{2}$)		1460 (1)

TABLE II

Sulphate	Lattice Oscillations			ν_3		ν_4		ν_1	ν_2	
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	132 (2s)	242 (2d)		387 (1)	447 (3d)	613 (1d)	747 (1)	976 (15)	1039 (1)	
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$					455 (4d)	613 (3d)		981 (15)	1046 (1s)	1101 (1b)
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	57* (3)	94 (4b)	252 (1d)	375 (1d)	447 (5b)	608 (2d)		986 (15)		1120 (1d) 1057 (1d)
$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$			330 (2d)		457 (4b)	603 (2d)	693 (1)	994 (15)	1085 (1)	1148 (1)
$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	145 (2s)	171 (2b)			457 (b)	623 (3d)	710 (1d)	982 (15)		
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$			333 (1d)	437 (4)	458 (3)	525 (2b)	613 (5b)	991 (15)	1084 (3)	1134 (6s)

*57 has a doublet structure

measured for the bands of the water of crystallisation in the sulphates are separately listed in Table III The results of the study of the water bands of

TABLE III

Substance	Maxima of Bands of Water of crystallisation				Remarks
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	3225 (2)	3337 (2)	3432 (6)	3543 (3)	
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	3226 (2)	3285 (3)	3458 (4)		Nisi's results are 3227 and 3445 (f, d) (f, v, d) Canals and Peyrot's values are 3230, 3322, 3404 and 3481
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	3207 (1)	3395 (5)			Canals and Peyrot report 3436
$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$.	3399 (3)	3467 (1)		
$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	3216 (6)	3285 (6)	3395 (7)		2527 2843 3090 are attributed (4) (1) (4) to NH_4 radical
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	3114 (1)		3375 (5)		Nisi's value is 3384 Canals and Peyrot report bands 2973 to 3207, 3377 and 3571
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$			3368 (6)	3476 (1)	3105 is assigned to NH_4 group

ammonium aluminium sulphate have also been included in this table, though the single crystal of this substance was not studied for the Raman effect. Figs 2, 3 and 4 in the Plate are reproductions of the spectrograms obtained in the case of the nitrates, the sulphates and of the water of crystallisation respectively. The intensities of the water bands recorded in Table III are relative to the arbitrarily assigned values of 15 for the corresponding symmetric oscillation at about 980 cm^{-1} of the SO_4 ion.

4 Comparison with earlier data

Tables IV and V bring together the results of the present and of earlier investigations. Table IV shows that the low frequency lattice oscillations in all the nitrates have been recorded for the first time except in the case of the line at 160 cm^{-1} which Krishnamurti observed as 155 cm^{-1} for lead nitrate. The frequency shifts of the fundamental oscillations of the NO_3 ion measured by Krishnamurti agree fairly well with the author's results. Some of the feeble lines with high frequency shifts recorded by Ananta-krishnan were found missing in the author's plates. It would seem that for recording such lines the powder method may be actually more efficient than the single crystal technique.

Regarding the sulphates (Table V) it can be seen that Nisi's results compare well with the present author's in many cases. The lattice line reported by Nisi at 189 cm^{-1} in potash alum with 3125.6 and 3131.7 excitations in the ultraviolet region did not appear with 4358 excitation, though several new low frequency shifts were obtained for other sulphates without difficulty. While Nisi reported only the single symmetrical oscillation in paramagnetic sulphates like ferrous sulphate, ferrous ammonium sulphate and manganese sulphate, the author has succeeded in obtaining all frequency shifts characteristic of the internal oscillations of the SO_4 ion, including the split components of the degenerate lines. The doubling of the symmetric ν_1 frequency reported by Nisi for potash alum has not been confirmed by the author's spectrogram. No such doubling is found either in ferrous ammonium sulphate, the other double salt examined in the present investigation.

TABLE IV

Nitrate	Worker	Lattice Oscillations					Frequencies of the NO ₂ ion						
Strontium	Krishnamurti						733	1056 5	1369 (1)	1400 (2)	1421 (2)	1537 (6)	1635 (1)
	Anantakrishnan						742 (4)	1058 5 (12)					
	Author	109 (6)	129 (1)	142 (1)	167 (2)	184 (6)	736 (4)	1057 (12)	1402 (1)	1423 (1)			
Barium	Krishnamurti						728 6	1048 7	1396				
	Author	82 (8)	134 (7)		160 (5)		728 (1)	1047 (12)	1383 (2)				
Lead	Krishnamurti		155				728	1046 8	1382				
	Anantakrishnan						730 (1)	1048 5 (12)		1420 (1)	1537 (1)	1614 (2)	1645 (1)
	Author	92 (10)	117 (3)	144 (2)	160 (4)		725 (1)	1046 (12)	1383 (1)	1460 (1)			

.. Discussion of Results

Low Frequency Lines.—In the present study of the nitrates, all the crystals yield a number of low frequency lines. These are very clear and strong, the intensity of the lowest frequency line in all cases being not far below that of the symmetrical oscillation. This may be ascribed to the very high optical anisotropy of the nitrate ion. In spite of the analogous crystal structure of the three nitrates, the lattice lines recorded are not identical either in frequency or in intensity. It appears probable that the masses and refractivities respectively of the different cations have an influence on these features.

As a contrast, the sulphates yield only faint lattice lines. This feature is not unexpected; the sulphate ion having spherical symmetry, only small polarisability changes would result from its rotational oscillations in the crystal lattice.

Internal Oscillations.—The nitrates studied show generally a diminution of the frequency shifts from the lighter to the heavier metal and there appears to be no dependence of their values on the ionic volumes of the cations. In the case of the sulphates, the frequency shifts of the principal inactive

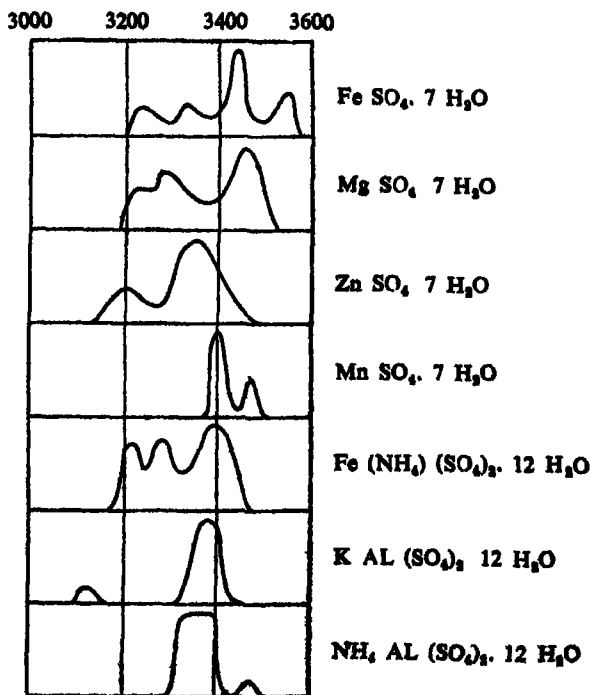


FIG. 1 Raman Bands of Water of Crystallisation

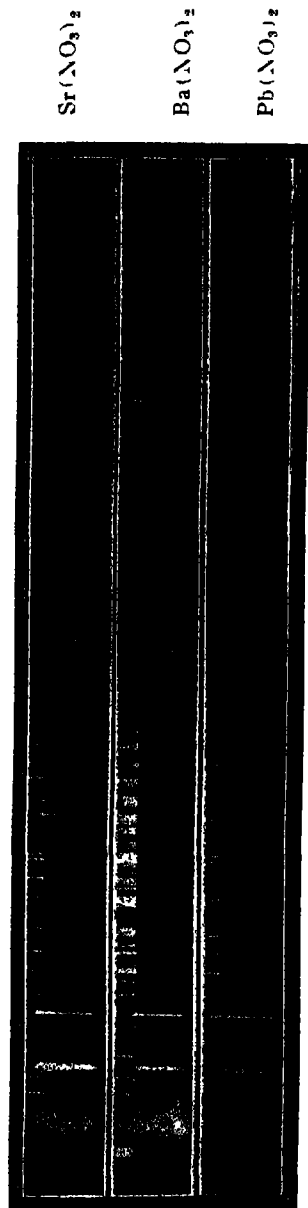


FIG 2

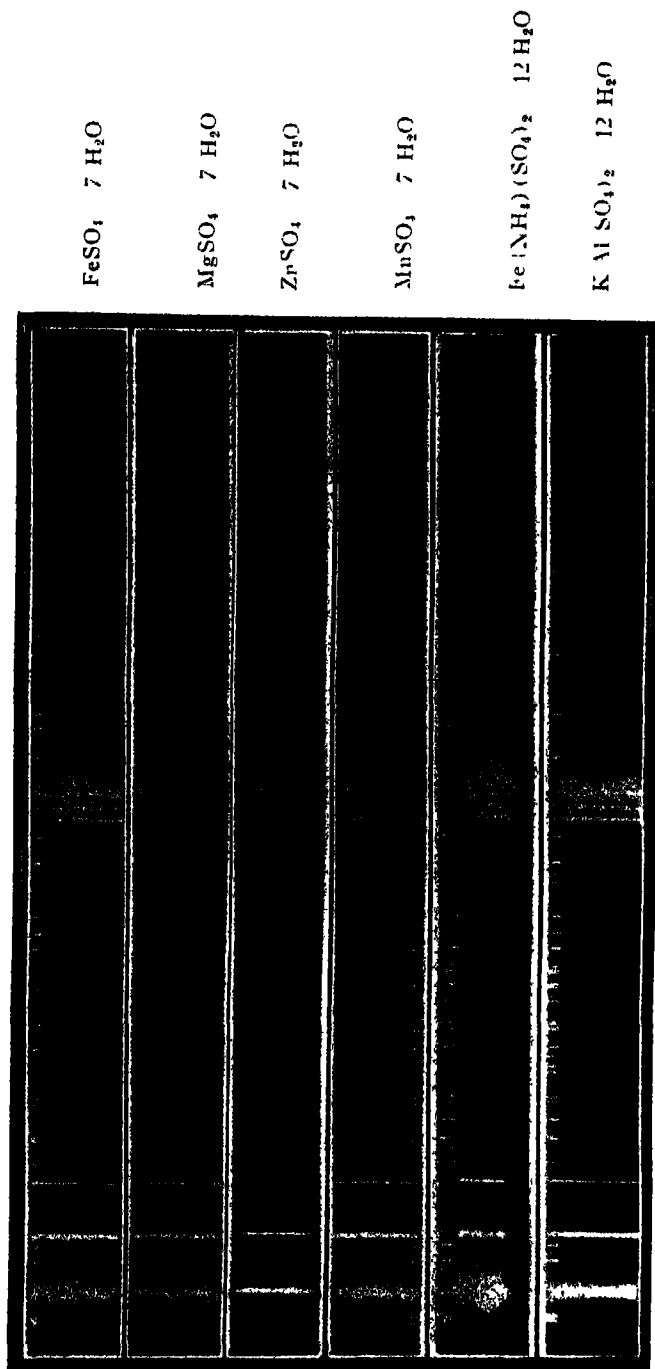


FIG 3

Raman Spectra of Single Crystals

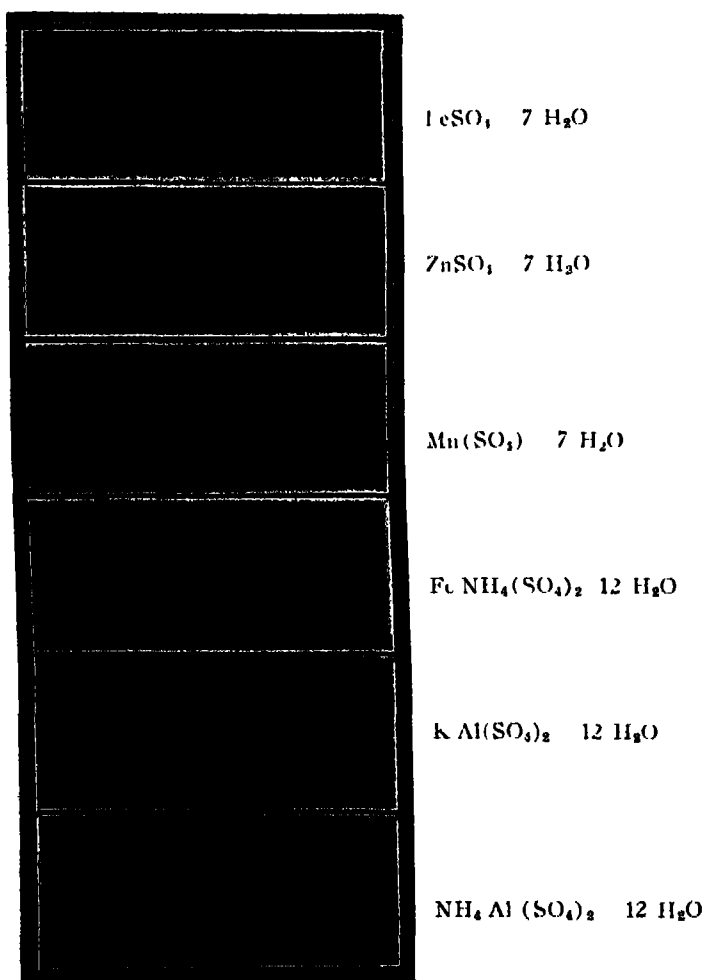


FIG. 4 Raman Bands of Water of Crystallisation

oscillation seems to show no relationship with either the atomic weight or atomic number. As regards the degenerate oscillations, their splitting has been clearly recorded for strontium and lead nitrates.

Water of Crystallisation.—Anantakrishnan, Nisi and particularly Nayar (1938) have studied the Raman bands of water of crystallisation in several crystalline hydrates. However, among the sulphates studied here the water bands have been recorded for the first time in ferrous sulphate, ferrous ammonium sulphate, manganese sulphate and ammonium aluminium alum. The characteristics such as the relative intensity, breadth and the frequency shifts of the bands have been represented in the form of a chart in Fig. 1 as has been done by Nayar. It is found that there is no direct relationship between the characteristics of the water bands even in single sulphates like those of iron, magnesium, zinc and manganese, though all of them have analogous crystal structure and contain the same number of molecules of water of crystallisation.

The author is indebted to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his inspiring guidance and to Mr. T. M. K. Nedungadi for invaluable help.

6 Summary

Using single crystals of strontium, barium and lead nitrates, several new low frequency lines have been recorded for the first time (see Table I in the paper). The sulphates examined in the form of single crystals have yielded all the frequency shifts characteristic of the internal oscillations of the sulphate ion, including some of the split components of the degenerate lines and also some new lattice frequencies. The paramagnetic sulphates have been shown to behave exactly like the non-paramagnetic sulphates (see Table II in the paper). The features exhibited by the water bands do not show any obvious correlation either with the number of molecules of the water of crystallisation or the crystal structure of the solid (see Table III in the paper).

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ON THE GEOMETRY OF THE QUANTUM REFLECTION OF X-RAYS IN DIAMOND

BY P RAMA PISHAROIY

• (From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE Raman effect in crystals, as is well known, arises from an exchange of energy and momentum between the crystal and a photon traversing it, the spectroscopic results of such exchange differing greatly in the two cases in which the vibrations of the crystal lattice following the encounter are respectively in the acoustic and optical ranges of frequency. In a series of papers which appeared in April and May 1940,^{1, 2, 3, 4} Raman and Nilakantan put forward evidence indicating that such quantum exchanges of energy and momentum occur also when X-rays pass through a crystal. If the excited vibrations of the lattice are of the acoustic class, that is, in the nature of elastic solid waves traversing the crystal, we have a *diffuse* scattering of the X-rays with relatively small alterations of frequency. On the other hand, when the vibrations are of the optical class, their frequencies lying in the infra-red region, we have a reflection of the incident monochromatic X-rays by the lattice planes of the crystal with altered frequency in specific directions which are, in general, different from those of the classical or Laue type of reflection. The theory of these effects has been discussed by Raman and Nath in two papers, 1940^{5, 6}. The geometric law obeyed by these dynamic reflections has been shown to be

$$2d \sin \psi \sin(\vartheta + \epsilon) = n\lambda \sin \vartheta \quad (1)$$

($n = 1, 2, 3 \dots$)

where, d - the crystal spacing,

2ψ - the angle between the incident and the reflected X-rays,

ϵ - the inclination of the dynamic stratifications to the static crystal planes,

and ϑ - the inclination of the phase waves (planes of constant phase) of the lattice oscillations to the static crystal planes

Though in the earlier X-ray literature references are found to "extra-spots" appearing in Laue diagrams, the true nature of the phenomenon as stated

above was first indicated and established by Sir C. V. Raman and his collaborators. In view of this and especially of the formal analogy between the new reflections and the Raman effect in crystals, they will be referred to in the course of this paper as "modified" or "quantum" or "Raman" reflections to distinguish them from the well-known unmodified or classical reflections of the Laue and the Bragg types.

2 *The Case of Diamond*

Though all crystals exhibit the phenomenon of modified X-ray reflection, the case of diamond is of extraordinary importance as it furnishes several crucial tests of the Raman-Nath theory of the phenomenon. In the first place, as has been shown by Raman and Nilakantan (1940⁷, and 1941⁸), the directions in which the modified reflections of the (111) planes of diamond are observed satisfy equation (1) in a very exact manner over a wide range of settings of the crystal, while they deviate widely from other formulæ which have been proposed. Further, the angle ϑ comes out as identical with the angle between the octahedral and cube faces of diamond. In other words the phase waves for the (111) reflection are parallel to the (100) planes, a most interesting result of which the physical significance becomes evident on an examination of a model of the diamond crystal. While the (111) planes are normal to the valence bonds joining the carbon atoms, the (100) planes bisect the angles between them, whereas both sets of planes contain the atoms belonging to the two interpenetrating lattices in separate layers interleaved with each other. Thus it is not surprising that an oscillation of these two lattices, relative to each other, normal to the (111) planes should have its phase waves parallel to the (100) planes.

The present paper deals with the purely geometrical aspects of the modified reflections by the (111) planes in diamond on the basis of formula (1) above. Granting that $\vartheta = 54^{\circ}44'$, in other words that the phase waves are parallel to the (100) planes, it follows immediately from considerations of symmetry that there should be three sets of phase waves, instead of one, namely, sets parallel to the (100) planes, the (010) planes and the (001) planes. The consequences of this idea are followed out in the paper. It is shown that they furnish a complete explanation of the phenomena of the streamers and the subsidiary spots accompanying the modified reflections (Raman and Nilakantan,^{3,7} 1940, 1941), as also the tripling of the spots observed in certain settings of the diamond by Jahn and Lonsdale⁹ (1941). Various other consequences of the formulæ are also worked out and found to be in accord with experimental facts.

3 *The circular shape of the Raman spots*

Before considering the phenomena of the streamers and subsidiary spots on the basis that there are three sets of phase waves as indicated above, we shall first consider the explanation of the fact that the modified reflections by the (111) planes appear in general as *round* spots instead of having an elliptic shape as in the case of the Laue reflections. We may put aside the suggestion—certainly not true in the case of diamond—that the round shape arises from any inherent “diffuseness” of the modified reflection. If we accept formula (1) as rigorously correct, *the modified reflections should be as sharp as the unmodified ones*, and the difference in shape of the spots should be merely a consequence of the difference in the geometric laws obeyed by them. We shall now proceed to show that this is actually the case.

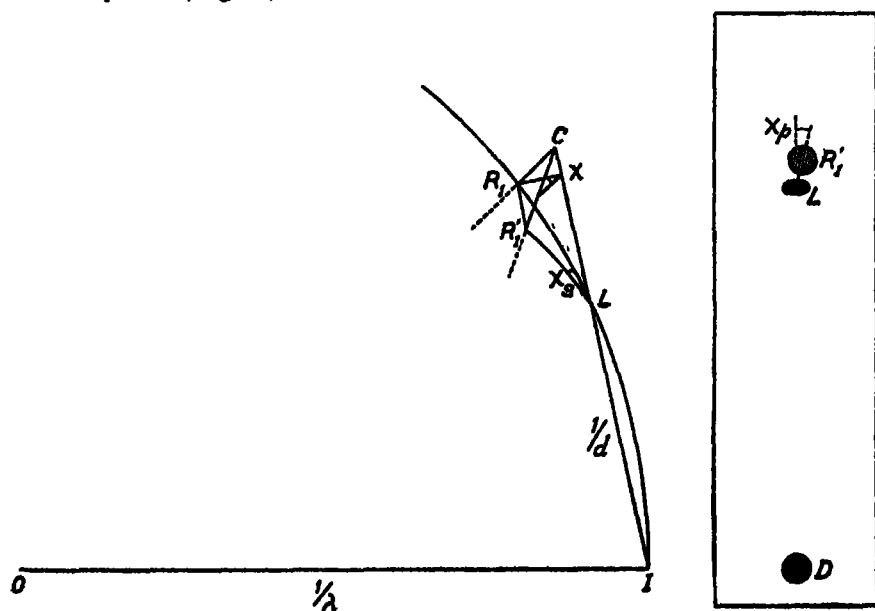
While a Laue reflection occurs with ‘white’ radiation, the Bragg and the Raman reflections occur with monochromatic radiation. In the Laue reflections neither the wave-length nor the angle of incidence is restricted; for the Raman reflections, owing to intensity considerations the wave-length must be considered as restricted while the angle of incidence is variable. For the Bragg reflections, both the wave-length and the angle of incidence are completely defined. Consequently when the incident pencil possesses a conical divergence only a narrow diametral section of the cone, normal to the incident plane, is operative for a Bragg reflection, while the entire cone is operative for the Laue and the Raman reflections. For the Laue reflection it is easily seen that the beam divergence in the incident-plane gets changed into a convergence while the divergence in the orthogonal plane is unaffected, thus rendering the spot elliptical. For a Raman reflection the total deviation (2ψ) of the ray remains sensibly a constant for small changes in the angle of incidence so that the original divergence of the beam remains unaffected by the reflection. Hence the Raman spot is circular with its diameter equal to the major axis of the Laue spot. Of course, this can happen only if the cone be of uniform intensity or if the exposure is sufficiently long. However, in practice the cone has a central intense core the intensity of the rest rapidly diminishing towards the edges. Therefore, in general, the modified spot is not crisp at the edges and its size is less than that of the unmodified spot.

The above discussion holds good only for an infinitely thin crystal. The effect of a small finite thickness ‘ t ’ of the crystal is to elongate the spots through a distance $t \tan 2\psi$, towards the direct spot.

4 Reflection not in the plane of incidence

The direction of the quantum reflection is found with the help of the sphere of reflection first introduced by Ewald. The vector $OI = 1/\lambda$ represents the direction of incidence and the vector IC represents the reciprocal lattice vector $1/d$ drawn normal to the crystal spacings concerned. When the point C lies just on the sphere of reflection drawn with O as centre and OI as radius, the Bragg reflection takes place and the angle OIC is the complement of the Bragg angle θ_B .

When θ , the glancing angle of incidence, is less than θ_B , the end C of the vector $1/d$ lies outside the sphere. No reflection is possible unless the phase waves creating the appropriate dynamic stratifications operate. As mentioned in § 2, Raman and Nilakantan have shown for diamond that these phase waves are transverse to the plane of incidence and inclined at $54^\circ 44'$ to the crystal spacings when the incident plane is a plane of symmetry—a (110) plane. For such an incident plane the reciprocal phase vector τ_1 lies in it, and OR_1 , the direction of the modified reflection, is also in the same plane (Fig. 1).



FIGS 1a-1b

FIG 1a OR_1 is in the direction of the Raman reflection when the plane of incidence is a (110) plane. OR_1' is the direction when the plane of incidence makes an angle χ with the 110 plane. FIG 1b shows the modified spot R_1' out of the incident plane as would appear on a photographic film normal to the incident X-ray pencil. L is the Laue spot.

However, when the crystal setting is slightly changed so that the plane of incidence is no longer a plane of symmetry, the reciprocal phase vector τ_1 cuts the sphere of reflection at a point R_1' , which is not in the incident plane. Hence the Raman reflection whose direction is given by OR_1' goes out of the plane of incidence

The angle R_1LR_1' on the sphere is the angle between the intersections of the planes ICR_1 and ICR_1' (the original and the final positions of the appropriate 110 plane of the crystal) with the surface of the sphere. χ is the angle between the planes ICR_1 and ICR_1' . If the angle R_1LR_1' is denoted by χ_r , we have

$$\tan \chi_r = \tan \chi \sin \theta,$$

where θ is the inclination of the tangent plane at L to the plane orthogonal to both the incident planes. This θ happens to be the glancing angle of incidence itself. The gnomonic projection χ_p of χ_r on the photographic plate normal to the incident pencil is given by

$$\tan \chi_p = \tan \chi_r \cos 2\psi = \tan \chi \sin \theta \cos 2\psi$$

Raman and Nilakantan actually looked for such a change in the position of the modified spot with change of the incident plane and their observations are in agreement with the above formula

The occurrence of such a modified reflection out of the plane of incidence in agreement with the above geometric formula is a striking confirmation, at least in the case of diamond, of the idea that the phase waves have a definite inclination and azimuth with respect to the crystal spacings giving rise to modified reflections

5 Explanation of streamers and subsidiary spots

That the 'streamers' and the subsidiary spots are consequences of the existence of three sets of phase waves parallel respectively to the (100), (010) and (001) planes was mentioned in § 2. When θ the glancing angle of incidence is different from θ_n , the three reciprocal phase vectors τ_1, τ_2, τ_3 corresponding to the three sets of phase waves naturally operate giving rise to modified reflections. τ_1, τ_2 and τ_3 are mutually perpendicular to each other and all are inclined at an angle of $54^\circ 44'$ to the reciprocal lattice vector $1/d$. To begin with we will consider the case $\theta > \theta_n$ and when one set of the phase waves is transverse to the plane of incidence their inclination being towards the incident pencil. This happens when the incident pencil is nearly along a trigonal axis, the reflection taking place from a set of (111) spacings normal to one of the other three trigonal axes. In this setting τ_1 is in the plane of incidence and points nearly towards the centre of the sphere of

reflection Let τ_1, τ_2, τ_3 cut the sphere of reflection at points R_1, R_2, R_3 . The directions of the modified spots are given by OR_1, OR_2 and OR_3 . If IC produced cuts the sphere of reflection at L , the direction of the Laue spot is OL . R_1 is in the plane of incidence and is the primary Raman reflection. The small finite divergence present in the incident beam makes IC sweep over a small angle in all directions so that R_1 is a nearly circular area while R_2 and R_3 are two very elongated ellipses. The appearance of these spots as will be recorded on a photographic plate normal to the incident pencil is represented in Fig 2b

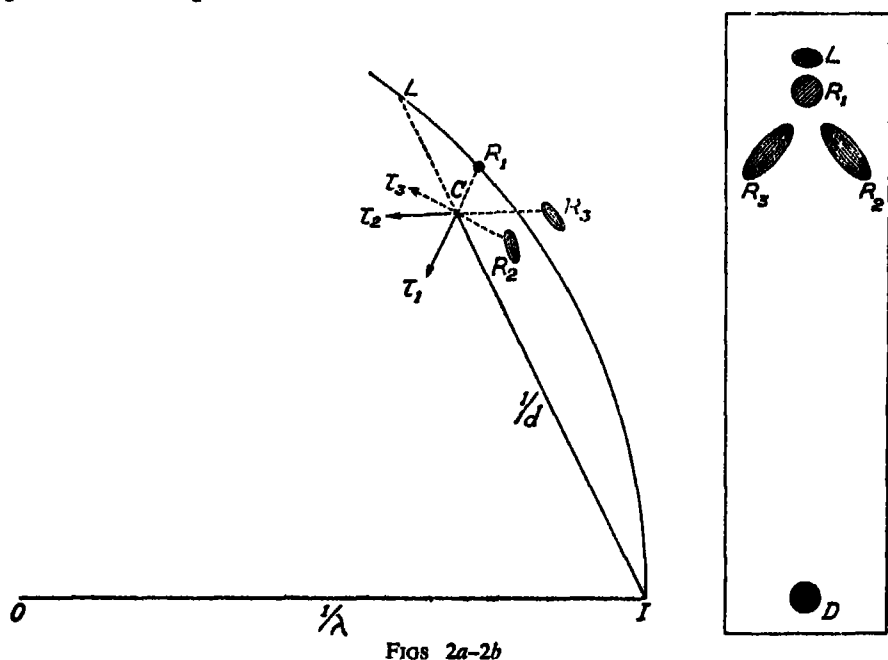
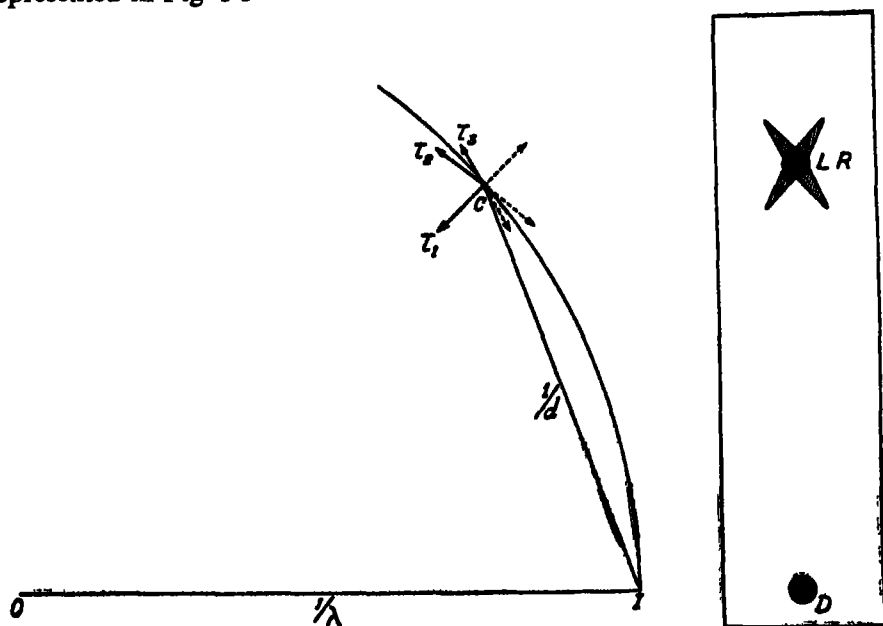


FIG 2a τ_1, τ_2, τ_3 are the three reciprocal phase vectors, τ_1 being in the plane of incidence. The diagram represents the case $\theta > \theta_B$. FIG 2b indicates the primary Raman spot R_1 and the two subsidiary spots R_2 and R_3 as will be recorded on a photographic film normal to the incident X-ray pencil. L is the Laue spot.

When the angle θ is further increased, C moves away from the surface of the sphere and the distance LR_1 as well as the size of the triangle $R_1 R_2 R_3$ increases.

When the glancing angle θ becomes equal to the Bragg angle θ_B , C lies just on the surface of the sphere and the plane containing τ_2 and τ_3 is only slightly inclined to the surface of the sphere at C . This inclination is nearly 13° for the particular setting of diamond we are considering, when copper radiations are used. The small divergence of the incident beam makes IC

sweep over a small angle in all directions so that the vectors τ_2 and τ_3 cut the sphere of reflection over long arcs nearly at right angles to each other. Every point on these arcs correspond to a possible direction of reflection so that we get four 'streamers' when the modified spot is just on the Laue spot. The appearance of the 'streamers' on the photographic plate is represented in Fig 3b

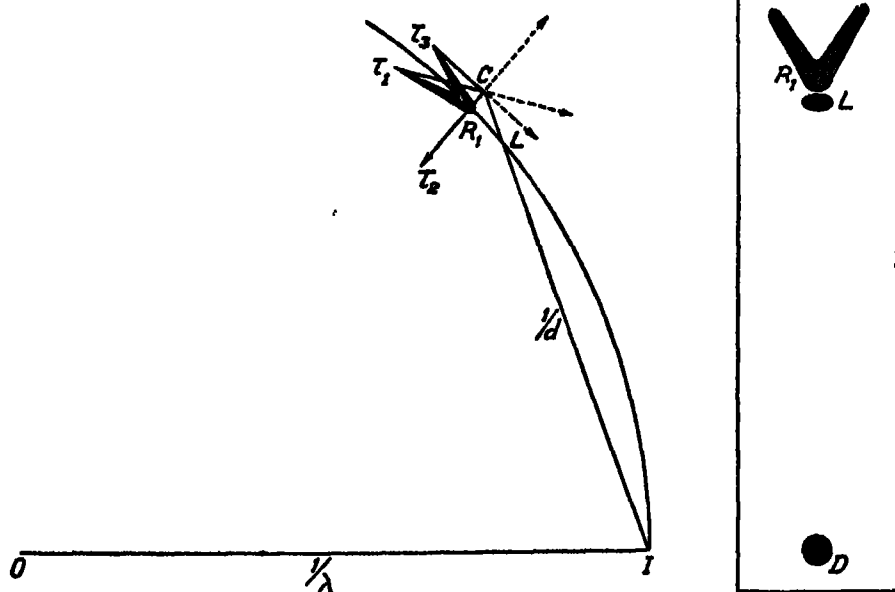


FIGS 3a-3b

FIG 3a Case $\theta = \theta_B$. τ_2 and τ_3 which are nearly on the surface of the sphere of reflection give rise to the streamers. FIG. 3b shows the streamers as they appear on the photographic film normal to the incident pencil. The Laue and the Raman reflections coincide.

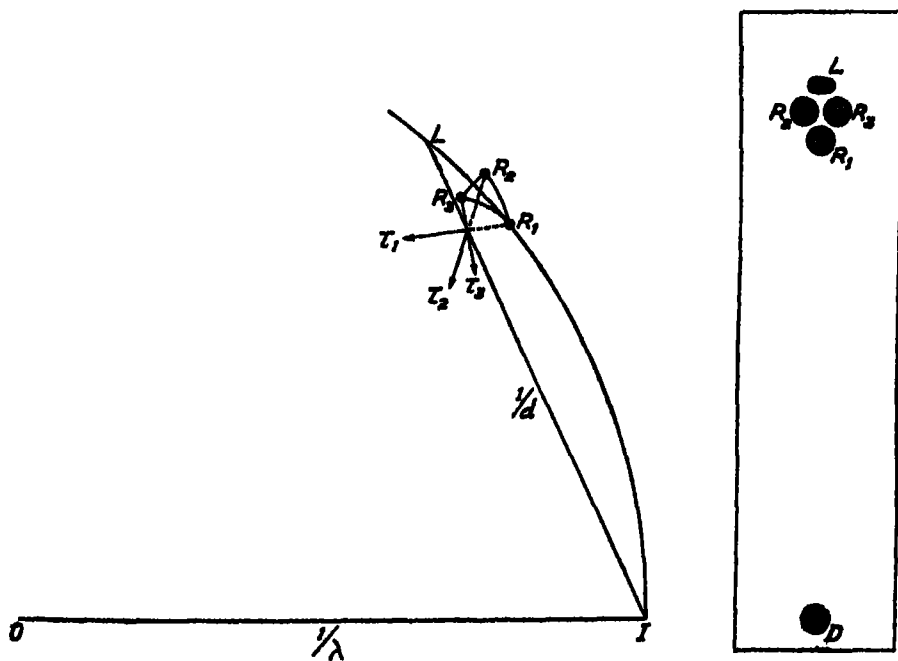
On decreasing the angle of incidence θ so that it is just less than θ_B , the end C goes out of the sphere of reflection. The Raman spot in the plane of incidence is given by R_1 , L being the position of the Laue spot. τ_2 and τ_3 cut the surface in R_2 and R_3 provided the distance of C from the surface of the sphere is very small. Since the inclination of τ_2 and τ_3 to the surface of the sphere is small, the divergence of the incident beam moves R_2 and R_3 over long arcs thus giving rise to the 'streamers'. When C is fairly distant from the surface of the sphere the vectors τ_2 and τ_3 leave off the surface of the sphere and therefore the 'streamers' disappear completely. This explains why the streamers are so sensitive to the crystal setting.

The disposition of the reciprocal phase vectors in the setting of Jahn and Lonsdale is different from what we have been considering so far. From



FIGS 4a-4b

FIG 4a Case $\theta < \theta_c$ FIG 4b shows the streamers starting from the modified spot R_1

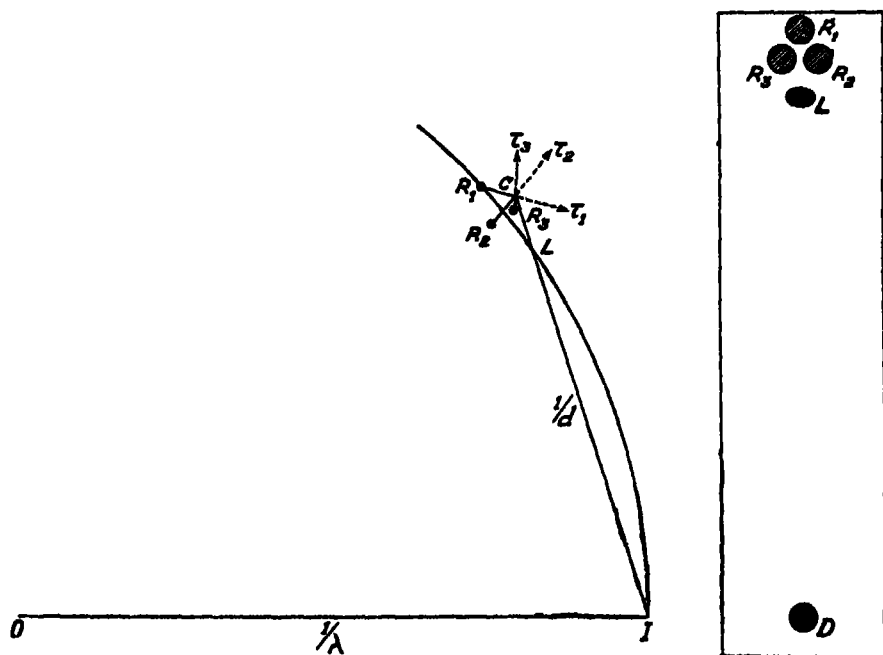


FIGS 5a-5b

FIG 5a Shows the relative disposition of the reciprocal phase vectors in the Jahn-Lonsdale setting for $\theta > \theta_c$. τ_1 is in the plane of incidence and meets the sphere of reflection at R_1 farther from the Laue direction L , than R_2 and R_3 . FIG. 5b indicates the triple spots as they appear on the photographic film.

a crystal model of diamond it is easily seen that the Jahn-Lonsdale setting is obtained from the setting, so far considered, by a rotation of the whole configuration through 180° with I C as axis

For $\theta > \theta_B$, C is inside the sphere and τ_1, τ_2, τ_3 cut the surface at the three points R_1, R_2, R_3, R_1 , the modified reflection in the plane of incidence being farther away from the Laue spot than the secondary spots R_2 and R_3 . The small uncertainty in the direction of O C due to the divergence of the incident pencil smears out the three reflections into partly overlapping spots, as all the three vectors τ_1, τ_2, τ_3 are having practically the same inclination to the surface of the sphere (This is not so for the setting previously considered) No streamers can occur when C is just on the surface of the sphere ($\theta = \theta_B$), for, all the vectors are considerably inclined (nearly 35°) to the surface, while for the other setting, two of the vectors are inclined at very small angles (about 9°) to the surface of the sphere. When $\theta < \theta_B$, C goes out of the surface and the disposition of R_1, R_2, R_3 changes



FIGS 6a-6b

FIG 6a Shows the reciprocal phase vectors in the Jahn-Lonsdale setting when $\theta < \theta_B$. τ_1 is in the plane of incidence. FIG 6b indicates the triple spots as they appear on the photographic film

such that R_1 , the modified reflection in the plane of incidence, is again farther from the Laue reflection than the subsidiary reflections. The size of the

triangle $R_1 R_2 R_3$ increases in either case with the distance of C from the surface of the sphere, i.e., as $\theta \sim \theta_B$ is increased. These are just the phenomena mentioned in the Jahn-and-Lonsdale note referred to before.

6 Quantitative Formulae

(a) *The secondary spots appearing in the first setting*—We will denote the modified spot in the plane of incidence by R_1 and the other two by R_2, R_3 (Fig. 2a). When R_1 is near the Laue spot the normal to the plane $R_1 R_2 R_3$ from C is inclined at an angle

$$A = \frac{\pi}{2} - \theta - \phi$$

with the reciprocal phase vector τ_1 giving rise to R_1 . Since CR_1, CR_2 and CR_3 are mutually perpendicular, the angle $R_2 \hat{R}_1 R_3 = 2\alpha$ is given by

$$\cos 2\alpha = \frac{1 - \cos^2 A}{1 + \cos^2 A}$$

As the spots are recorded on a photographic plate held normal to the incident ray, we are interested in the gnomonic projection of this angle on the plane tangent to the sphere at I. If $2\alpha_p$ be the value of this angle we have

$$\tan \alpha_p = \tan \alpha \cos 2\psi,$$

where 2ψ is the angle between OI and OR_1 . For diamond $\phi = 54^\circ 44'$ for the (111) reflection of copper K_α radiation $\theta_B = 21^\circ 58'$. When the crystal is near the Bragg setting $\theta + \phi$ is practically $2\theta_B$. Substituting these values $2\alpha_p$ works out to be nearly 71° . As θ increases 2ψ also slightly increases so that the angle $2\alpha_p$ decreases as we move more and more from the Bragg setting.

The distance $R_1 R_2$ or $R_1 R_3$ is easily calculated in terms of the distance of C from the surface of the sphere of reflection. Let the directions of the vectors τ_1, τ_2, τ_3 be taken as the co-ordinate axes. Then the direction cosines of p , the normal drawn from C to the plane $R_1 R_2 R_3$ are $\cos A$,

$\sin A \cos \frac{\pi}{4}$, and $\sin A \sin \frac{\pi}{4}$. Hence,

$$R_1 R_2 = p \left(\frac{2}{\sin^2 A} + \frac{1}{\cos^2 A} \right)^{\frac{1}{2}}.$$

Now

$$p = \frac{1}{d} (\theta - \theta_B) \cos \theta.$$

Therefore the angular distance, between the main Raman spot R_1 and one of the subsidiary spots, is

$$R_1 R_2 / \lambda = \frac{\lambda}{d} (\theta - \theta_B) \cos \theta \left\{ \frac{2}{\sin^2 A} + \frac{1}{\cos^2 A} \right\}^{\frac{1}{2}}.$$

From equation (1) it can be shown with a little manipulation, that the angular distance of the main Raman spot R_1 from the Laue spot is given by

$$LOR_1 = 2(\theta - \theta_B)(1 + \cot \theta \tan \theta)^{-1}$$

Hence the ratio of the angular distance between the main spot and a subsidiary spot to that between the main spot and the Laue spot simplifies on substituting the values involved in the copper K_α reflections from the (111) planes of diamond to the approximate value

$$0.68 \operatorname{cosec} A$$

A is as before ($90^\circ - 54' 44'' - \theta$) and is taken as small in the simplification. When $\theta = 23^\circ 12'$ for which the subsidiary spots are distinct, this ratio is nearly 3, a value which agrees very well with the experiments of Raman and Nilakantan. The formula also shows how the size of the triangle formed by the three spots increases as the distance of the main spot from the Laue spot is increased.

(b) *The streamers*—When θ is just less than θ_B the vectors τ_2 and τ_3 are very little inclined to the surface of the sphere (Fig. 4). The inclination of the plane containing τ_2 and τ_3 to the surface of the sphere at R_1 is as

before

$$A = \frac{\pi}{2} - \theta - \theta$$

Due to the small divergence $\delta\theta$ in the plane of incidence the end point C of the vector IC moves through a distance $IC \delta\theta$. Consequently the vectors τ_2 and τ_3 sweep out arcs on the sphere of reflection and these arcs determine the streamers. The angle 2α between the streamers is as before given by

$$\cos 2\alpha = \frac{1 - \cos^2 A}{1 + \cos^2 A}$$

The gnomonic projection of this angle on the photographic plate is given by

$$\tan \alpha_p = \tan \alpha \cos 2\psi.$$

Substituting the appropriate data for diamond, we get $2\alpha_p$ to be nearly 71° which is in good agreement with the observed value of about 69° .

The length of the streamers for an uncertainty $\delta\theta$ in the orientation of the reciprocal lattice vector,—i.e., for a divergence of $\delta\theta$ in the incident beam is calculated as follows. The angle β made by the vector τ_1 or τ_3 with the surface of the sphere at R_1 is given by

$$\sin \beta = \sin A \cdot \sin \frac{\pi}{4}.$$

When the end of the vector IC is lifted above the surface of the sphere of reflection, the vectors τ_2 and τ_3 cut through the great circles containing

them. The angle γ of the arc cut on one of them as a result of this lift is given by

$$\gamma \left(\beta - \frac{\gamma}{2} \right) = \frac{\lambda}{d} \cos \theta_B \delta \theta,$$

where $\delta \theta$ is the angle through I C is rotated, λ and d being the wave-length and the crystal spacing respectively. Substituting the values for the reflection of Cu K_α radiation from the (111) planes of diamond, we obtain

$$\gamma \simeq 4.5 \delta \theta$$

Hence a total divergence of one degree in the incident beam will produce a streamer about 4.5 degrees long. The height of the segment of the great circle containing τ_2 , above the vector τ_2 , in the correct Bragg setting is only

$$\frac{1}{\lambda} \left(1 - \sin^2 \frac{\beta}{2} \right)$$

Therefore when $(1/d) \cos \theta (\theta_B - \theta)$ is equal to this quantity, the vectors τ_2 and τ_3 are lifted cleanly off the surface of the sphere and the streamers disappear completely. The magnitude of $(\theta_B - \theta)$ —the angular tilt of the crystal from the correct Bragg setting—required to bring about this disappearance of the streamers works out to be nearly 2° for the diamond case we are dealing with.

(c) *The spots in the Jahn-Lonsdale setting*—In this setting the triangle formed by the components of the triple spot has its apex in the plane of incidence and always away from the Laue spot (Fig. 5). The angle made by τ_1 with the normal to $R_1 R_2 R_3$ is given by

$$B = \frac{\pi}{2} + \theta - \delta,$$

(while for the other setting it is $\frac{\pi}{2} - \theta - \delta$). The angle $R_2 \hat{R}_1 R_3 = 2\alpha'$ is given by

$$\cos 2\alpha' = \frac{1 - \cos^2 B}{1 + \cos^2 B}.$$

If $2\alpha'_p$ be the gnomonic projection of this angle on the photographic plate,

$$\tan \alpha'_p = \tan \alpha \cos 2\psi,$$

where 2ψ is the angle between the incident pencil and the modified reflection in the incident plane. Substituting the data for the particular case of diamond we are dealing with, $2\alpha'_p$ works out to be about 42° , when $\theta \sim \theta_B$ is small. As $\theta - \theta_B$ changes sign there is no change in the angle $R_2 R_1 R_3$, but however, the triangle gets inverted.

The angular distance R_1R_2 is given by

$$\frac{\lambda}{d} (\theta - \theta_B) \cos \theta \left\{ \frac{2}{\sin^2 B} + \frac{1}{\cos^2 A} \right\}^{\frac{1}{2}},$$

and the angular distance LR_1 is nearly equal to

$$2(\theta - \theta_B)(1 - \cot \theta \tan \theta)^{-1}$$

Therefore the ratio of R_1R_2 to LR_1 is, to a first approximation,

$$0.24 \left(\frac{2}{\sin^2 B} + \frac{1}{\cos^2 B} \right)^{\frac{1}{2}}.$$

For settings near the Bragg setting this works out to be nearly 0.60. The photograph appearing in the *Nature* note by Jahn and Lonsdale suggests this value.

My sincere thanks are due to Sir C. V. Raman, F.R.S., for his invaluable help in the course of this work. In addition, I wish to record my thanks to Dr. P. Nilakantan for his very useful suggestions.

7 Summary

The paper deals with the purely geometrical aspects of the Raman reflections from the (111) planes of diamond based on the Raman-Nath formula. The round shape of the spots obtained over a wide range of the setting of the crystal as contrasted with the elliptic shape of the Laue reflections is explained as a purely geometrical consequence of the divergence of the incident pencil and the special law of the reflection. The appearance of quantum reflections outside the plane of incidence in cases when it is not a plane of symmetry is worked out quantitatively and the agreement with observation is a striking evidence of the definite orientation of the phase waves associated with the lattice vibrations in this case. From considerations of symmetry three sets of phase waves, parallel respectively to the three (100), (010) and (001) planes, are postulated instead of the only one transverse to the plane of incidence. The streamers and the two subsidiary spots accompanying the modified reflection (Raman and Nilakantan), their behaviour with changes of the crystal setting, the tripling of the spots in a particular setting (Jahn and Lonsdale), its changes with changes in the angle of incidence—all these different phenomena are shown to be geometrical consequences of the above idea. The various quantitative formulæ derived are found to be in accord with experimental facts.

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THE BRIGHTNESS OF THE ZENITH SKY DURING TWILIGHT

BY M. W. CHIPLONKAR, M.Sc

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(Communicated by Dr. K. R. Ramanathan)

A DETAILED application of Rayleigh's theory of molecular scattering of light to the problem of day-sky illumination was made many years ago by L. V. King¹ who obtained results which in their main features were borne out by the observations of the Smithsonian workers. Gruner² in a series of papers extended the application to include not only low angles of the sun above the horizon but also considered early twilight, when the sun is a few degrees below the horizon. He also made actual observations of the changes in colour of the various parts of the sky during twilight. Ramanathan³ made calculations of the intensities of different parts of the sky, for a high level station (Simla, 7000 ft above sea level) and for early twilight based on the assumption that the phenomenon of twilight is due to the scattering of sunlight by air molecules and the results agree as well as may be expected with Dorno's observations of sky brightness made in clear weather in Switzerland.

Recently Fessenkoff⁴ and Link⁵ have extended the application a step further and tried to connect the measured brightness of the zenith sky when the sun is below the horizon, with the density of air at different levels in the upper atmosphere. More recently, Hulburt⁶ has made a similar attempt to derive the distribution of air density with height by photometric measurements of the brightness of the zenith sky and the luminous flux across a vertical plane from the twilight horizon.

In 1937 a simple photometer was developed at the Colaba Observatory, Bombay, in order to carry out measurements of the intensity in the visual region of the zenith sky during twilight. An account of the work done is given below; and a tentative distribution of temperature with height in the upper atmosphere is deduced assuming the scattering at the time of twilight to be mainly primary scattering.

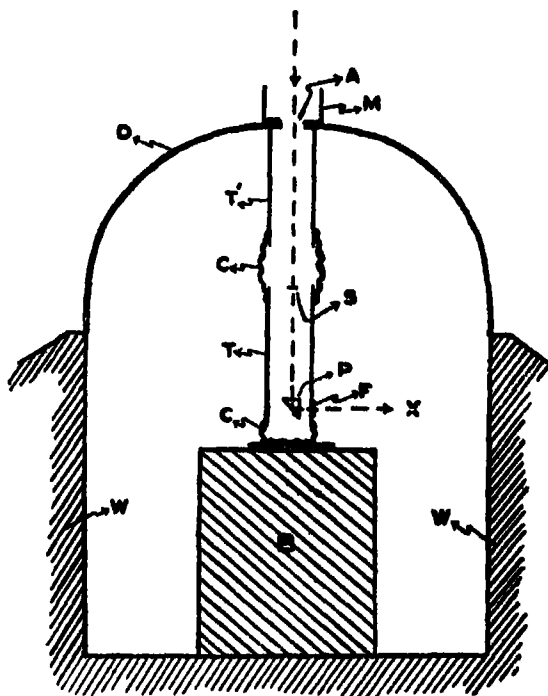


FIG. 1

- | | |
|----------------------------|---|
| <i>W</i> -Wall | <i>S</i> —Screen coated with magnesium oxide |
| <i>D</i> -Dome | <i>A</i> —Aperture in the dome |
| <i>B</i> -Stone pillar | <i>M</i> —Metal cylinder |
| <i>T</i> —Wooden tube | <i>X</i> —The position of the eye of the observer |
| <i>T'</i> —Metal tube | <i>C</i> —Black cloth |
| <i>P</i> —Reflecting prism | <i>F</i> —Colour filter |

Experimental

Fig. 1 shows a diagrammatic sketch of the experimental arrangement set up for making visual photometric measurements of the zenith sky. A is a rectangular hole in the top of the dome D, through which the scattered light from the zenith sky is let into the dark room. After passing down the two tubes T' and T, it is reflected in a horizontal direction by means of a right-angled prism P so that the observer, with his eye at X, could view a portion of the zenith sky and follow the gradual changes in its brightness. The details of the photometer are shown in Fig. 2. A small electric lamp run on a six volt accumulator illuminates the screen S, coated with magnesium oxide and supported by means of thin wires in the centre of the tube T. The current in the lamp can be varied continuously, so that the illumination

on the screen varies from zero to a certain maximum value. A precision milliammeter in the circuit indicates the current. Thus the current reading is a measure of the illumination on the screen and in turn when matched against the sky, of the brightness of the sky.

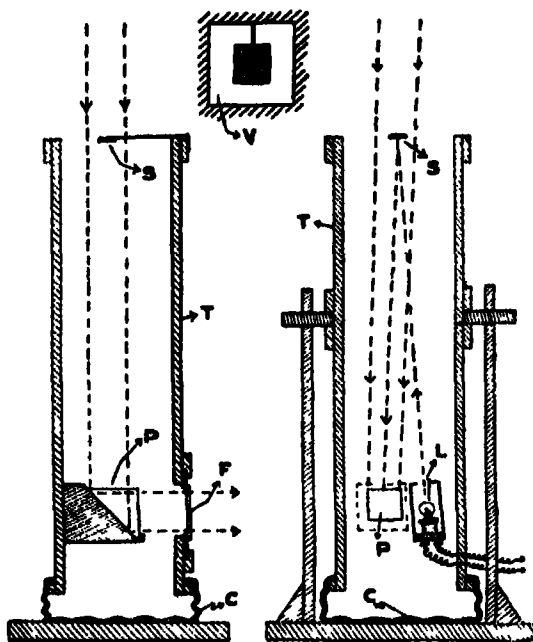


FIG 2

S—Screen coated with magnesium oxide

T—Wooden tube

P—Reflecting prism

F—Colour filter

C—Black cloth

L—Electric lamp

Measurements were taken with two colour filters, red (Schott and Genossen RG₁, 2.1 mm) and green (Schott and Genossen VG₁, 2.0 mm) which were brought in turn in the horizontal path of light. The field of view is shown as an inset at V in Fig 2. The metal tube T', the wooden tube T, and everything else inside the photometer which could scatter light were painted dull black to ensure against stray reflections.

Readings were taken with this arrangement on every clear and moonless evening during the period December 1937 to March 1938. The illumination caused by the lamp even at its brightest was far too weak compared to the scattered light from the zenith sky, until the sun sank a few degrees below the horizon. The first reading could therefore be taken with the red filter

only when the sun was below the horizon by about 5° , and with the green filter, by about 6° . In order to accustom the eyes to the very feeble light, the observer used to keep himself in the dark for about ten minutes before starting the measurements and it was possible to continue the measurements well into the night.

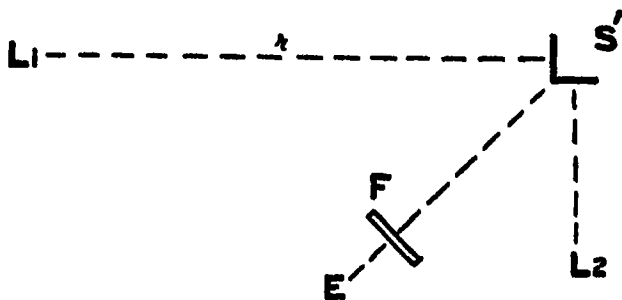


FIG 3

Calibration of the electric lamp—The electric lamp of the photometer was standardised in the laboratory against a Kodak acetylene lamp, using the same two colour filters. For this purpose, a simple arrangement shown in Fig 3 was adopted. S' is a rectangular metal screen bent sharply at right angles in the middle, and coated with magnesium oxide on the outside. The two sides of the screen were illuminated normally by the two sources under comparison and were observed from O , through each filter in turn. The distance between the acetylene lamp L_1 and the screen S' was changed, while a corresponding change in the intensity of the lamp L_2 was made by varying the current in it till the two portions of the screen were matched. Thus the readings of the currents flowing in L_2 were converted into corresponding values of K/r^2 where r is the distance between L_1 and S' , and K is a constant depending upon the candle power of the lamp L_1 , the transparency of the colour filter used, the sensibility of the human eye for the particular colour and the reflection coefficient of the screen S' . In the earlier stages of the calculation, values of $1/r^2$ only were used; these were later multiplied by K . Calibration curves were drawn for the two colour filters and used for converting the daily readings of the current into intensities.

For every day of observation two curves, one for each filter, were drawn showing the variation of $\log 1/r^2$ with time. In order to find a mean curve for all days of observations (the individual curves show little change from day to day) the abscissa was changed from *time after sunset* into '*depression of the sun below the horizon in degrees*'. The two mean curves thus derived are shown in Fig. 4

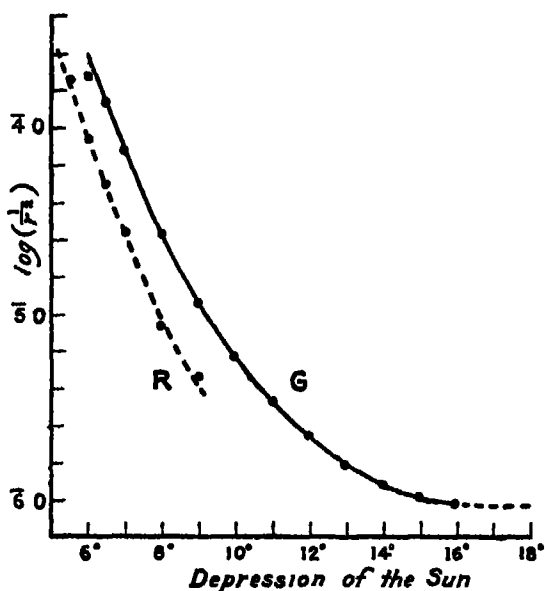


FIG 4

Conversion to absolute values—In order to find the value of K the following procedure was adopted. Since the candle power of the Kodak acetylene burner is 1 552, the illumination at the Magnesium Oxide screen, placed at a distance r from it, is $1 \cdot 552/r^2$, and its brightness $1 \cdot 552 \times 0 \cdot 97/\pi r^2$ candles cm^{-2} , 0 97 being the coefficient of diffuse reflection (or albedo) of the magnesium oxide screen. This brightness will be reduced when the screen is viewed through the green filter owing to a number of causes, by a fraction which can easily be calculated from —

- (1) the known transmission coefficients of the filter for different wavelength regions,
- (2) the distribution of energy in the spectrum of the source, and
- (3) the luminosity (visibility) curve of radiant energy

It was found by graphical computation that the factor by which the intensity of illumination of the acetylene lamp was reduced by the green filter was $1/5 \cdot 35$. Thus the brightness of the screen at a distance r will be $1 \cdot 552 \times 0 \cdot 97/5 \cdot 35 \times \pi r^2$, candles cm^{-2} . The constant K referred to above is thus equal to $1 \cdot 552 \times 0 \cdot 97/5 \cdot 35 \times 3 \cdot 14 = 0 \cdot 0896$ (for green filter)

Thus multiplying by 0 0896 we get the values of the brightness in absolute units, of the zenith sky for different depressions of the sun below the

horizon The corresponding value of K when the red filter is used is 0.0664 The values of brightness are given in columns 5 and 6 of the following table

For the sake of comparison, the absolute values of the brightness of the zenith sky measured at Bombay and those measured by Link⁷ at Rysy (2300 m) are brought together in the following table The original values of Link were expressed in magnitudes taking the sun as the standard They have been converted into magnitudes taking the standard candle as the standard (column 3) and then expressed as logarithms of the ratios of the brightness of the zenith sky (I_m) to that of a standard candle at a distance of one metre (I_o) (column 4). It is assumed⁸ in these calculations that the star magnitude of the sun is -26.7 and that of the standard candle at a distance of one metre is -14.2

TABLE I

Depression of the sun below horizon in degrees	Measurements at Rysy		$-0.4m = \log_{10} \frac{I_m}{I_o}$	Measurements at Bombay	
	Brightness of the zenith sky per sq degree in the green in magnitudes relative to —			Logarithm of (brightness of the zenith sky/brightness of the standard candle)	
	the sun	the standard candle		Green	Red
6	22 85	10 35	5 8600	5 3311	6 7897
7	24 35	11 85	5 2600	6 8211	6 2543
8	25 60	13 10	6 7600	6 3811	7 7674
9	26 65	14 15	6 3400	6 0181	7 4786
10	27 50	15 00	6 0000	7 7051	
11	28 35	15 85	7 6600	7 4921	
12	29 05	16 55	7 3800	7 3101	
13	29 70	17 20	7 1200	7 1651	
14				7 0541	
15				8 9791	
16				8 9521	

When the sun is 6° below the horizon the zenith sky at Rysy appears to be much brighter (about 3.38 times) than that at Bombay This ratio, however, gradually gets less and less upto about 12° At 13° , the zenith

sky at Bombay becomes slightly brighter than that at Rysy. The brightness of the zenith sky at Bombay in star magnitudes when the sun is 16° below the horizon is given by $-0.4m = 8.9521 = -7.048$, that is, $m = 17.6$.

In Table I of his paper "Sur les variations de la brillance du ciel nocturne" Jean Dufay⁹ has given a number of values of the brightness of the night sky for different seasons of the year, measured during the period 1922-1926. The values are expressed in photographic star magnitudes. The mean of all these values is 4.31 photographic star magnitudes. This has to be increased by 0.25 in order to get the visual star magnitudes, viz., 4.56. Comparing as before with the brightness of the standard candle, we obtain for the brightness of the night sky in visual star magnitudes $4.56 + 14.2 = 18.76$.

Similar measurements of Bauer, Danton and Langevin¹⁰ at Mont Blanc give a mean value of 4.27 for the brightness of the zenith sky in terms of visual star magnitudes per square degree, when the sun was $25-29^\circ$ below the horizon. With reference to the standard candle at a distance of one metre this becomes 18.47.

Both these estimates of brightness are much smaller than Link's value of 17.2 at $\theta = 13^\circ$, and the present measurement of 17.6 at $\theta = 16^\circ$, although in both the latter measurements part of the radiation is cut out by the green filter used.

Calculation of upper air temperatures—The curves of Fig. 4 showing $\log 1/r^2$ against the depression of the sun below the horizon can be utilised as shown by Link to deduce approximate values of upper air temperatures assuming the composition of air to remain constant with height. Let p be the pressure at height h , in the atmosphere. When the scattering of sunlight is confined to the air above h , b , the brightness of the zenith sky may be taken to be proportional to p , which is proportional to the air mass above. Let h change to $(h + dh)$, p to $(p - dp)$, and b to $(b - db)$. Then we may write

$$db/b = dp/p \quad (1)$$

Also dp can be expressed as

$$dp = -g\rho/dh = -gpm \cdot dh/RT$$

where T is the average temperature of the layer dh , m , the mean molecular weight of air, g , the acceleration due to gravity and R , the gas constant. Therefore,

$$dp/p = -gm \cdot dh/RT. \quad (2)$$

Also, $h = r(\sec \theta - 1)$, where r is the radius of the earth, and θ the depression of the sun below the horizon. Therefore, $dh = r \sec \theta \tan \theta d\theta$.

Substituting this in (2) and using (1) we get

$$db/b = dp/p = -mgr \sec \theta \tan \theta d\theta/RT$$

or

$$1/b \quad db/d\theta = - \beta \sec \theta \tan \theta, \text{ where } \beta = mgr/RT$$

This last relation has been used by F Link to derive the density distribution in the upper air. It shows that β represents the slope of the curve obtained by plotting $1/b \quad db/d\theta$ against $\sec \theta \tan \theta$. Further since $\beta = mgr/RT$ wherein all the quantities except m and T are known, we can deduce the values of T if we assume m to remain constant

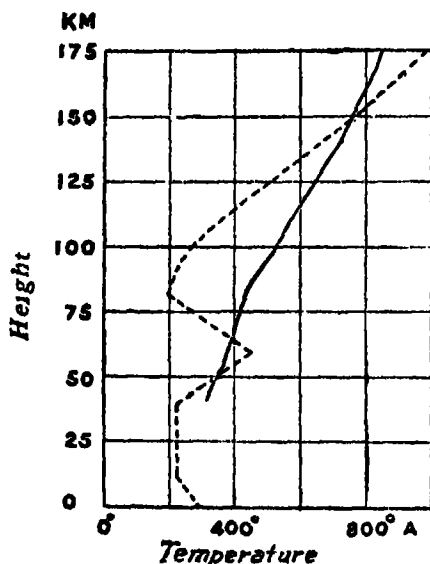


FIG 5

The distribution of temperature with height in the upper atmosphere
Continuous curve obtained from the twilight measurements at Bombay
Broken curve according to Godfrey and Price

As the brightness of the zenith sky could be measured over a much longer period with the green filter than with the red, a rough estimate of the distribution of temperature with height was deduced from the green curve only. The results are shown in Fig 5. For the sake of comparison the distribution of temperature with height based on different experimental and theoretical considerations given by Godfrey and Price⁷ is shown in the same figure. In piecing together the latter curve, information from widely different sources such as balloon ascents, propagation of sound waves, earth's magnetism, oscillations of the free atmosphere, observations of the meteors, and reflections of the radio waves, has been utilised. On the other

hand the former curve, although based on the results of a single series of experiments, covers a considerable range of the atmosphere and brings the principal feature of the other curve. However, since at any time large thicknesses of the atmosphere are involved in scattering the sunlight and since the calculated result depends on the estimate of the rate of variation of the brightness, it is to be expected that the temperature distribution curve based on the observations of scattered light¹² will lack in details. Moreover, the effect of secondary scattering has been neglected.

My thanks are due to Dr K R Ramanathan of the India Meteorological Department for having suggested the problem and providing the necessary facilities for work at the Colaba Observatory, Bombay, during the year 1937-38

Abstract

A visual photometer is described for measuring the brightness of the zenith sky during twilight. The results of measurements made with it at Bombay on a large number of clear moonless evenings during the period December 1937 to March 1938 are discussed. A red filter RG₁ (Schott and Gen) and a green filter VG₁ (Schott and Gen) were used. With the latter, it was possible to continue observations even when twilight conditions had completely ceased. The variations in brightness agree with a relation proposed by Link, namely, $dI/I = \beta \sin \theta \sec^2 \theta d\theta$, where I is the brightness of the zenith sky, θ the angular depression of the sun below the horizon and β a constant. If the brightness is due only to primary scattering from the atmosphere illuminated by sunlight, it is possible to connect β with the temperature of the atmospheric layer responsible for the scattering. The difficulty however is to ascertain to what extent secondary scattering is important.

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CHEMICAL EXAMINATION OF THE FIXED OIL DERIVED FROM THE SEEDS OF *LALLEMANTIA* *ROYLEANA* BENTH. OR *TUKHM-I-MALANGA*

BY BRAJ KISHORE MALAVYA AND SIKHIBHUSHAN DUTT

(Chemistry Department, University of Allahabad)

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LALLEMANTIA ROYLEANA BENTH commonly known as *Tukhm-i-malanga*, is an annual herb belonging to the Natural Order of Labiatae. It is cultivated throughout Northern India for the sake of its highly medicinal and mucilaginous seeds which are widely used as remedial agents in various ailments and also as an added palatable ingredient in cooling drinks and 'sher-bets', chiefly by the Muslims.

The seeds are about 1/12 inch in length, 1/16 inch in breadth, dark-brown to black in colour, smooth, three angled and tapering towards the umbilicus which is marked by a tiny white spot. When moistened with water, the seeds become coated with a voluminous and translucent mucilage. The taste of the moistened seed is bland and somewhat spicy.

According to Day,¹ a poultice of the moistened seeds is found useful in abscesses and inflammations. They are considered to be cephalic, astringent, cardiac tonic and carminative by Dymoch.² Kirtikar and Basu³ describe the seeds as cooling and sedative.

The chemical constituents of the seeds which impart to it the medicinal properties described above are not known, and the seeds do not seem to have been chemically examined as yet. In the present investigation the seeds have been found to contain 10.8 per cent of a fixed oil, and one should not be surprised if this oil is responsible for their medicinal properties.

Experimental

5 Kilos of the crushed seeds were extracted by hot benzene in a large extraction flask, and after removal of the solvent by distillation, the crude fixed oil was left behind as a bottle green and somewhat opalescent liquid. It was purified by treatment with animal charcoal and Fuller's earth and was ultimately obtained as a transparent light green oil. On further examination it was found to be a semi-drying oil having the following physical and chemical constants.

TABLE I
Physical and Chemical Constants of the Oil

Specific gravity at 32° C	0.9162
Refractive index at 30° C	1.4212
Acid value	2.07
Saponification value	191.20
Acetyl value	Nil
Hehner value	89.3
Iodine value	108.5
Unsaponifiable matter	0.28%

250 Grams of the oil were saponified in the usual manner with alcoholic caustic potash and the soap thus formed freed from the solvent and dried in the steam oven. It was then extracted exhaustively with ether in order to recover the unsaponifiable matter. After this it was decomposed with dilute hydrochloric acid in presence of petroleum ether and the petroleum ether solution of the fatty acids freed from the solvent by distillation. The fatty acids obtained in this way had the following physical and chemical constants

TABLE II
Physical and Chemical Constants of the Mixed Fatty Acids

Consistency	liquid at 20° C
Specific gravity at 22° C	0.9128
Refractive index at 30° C	1.4102
Neutralisation value	202
Mean molecular weight	277.9
Iodine value	122

The mixture of fatty acids were then separated into saturated and unsaturated acids by Twitchell's⁴ lead salt method and the following table gives the percentage, iodine value and the mean molecular weight of the saturated and unsaturated acids —

TABLE III
Saturated and Unsaturated Acids

Acid	% in mixed acids	I V	Neutralisation	Mean M W
Saturated	14.3	10.5	211.5	264.8
Unsaturated	85.7	140.6	199.7	280.3

Examination of the unsaturated acids — The constituents of the unsaturated acids were determined by the method originally suggested by Eibner

and Muggenthaler⁵ and later on worked by Jameson and Baughman⁶ According to this method the bromine addition products of the unsaturated acids were prepared and separated as follows —To a known weight of the unsaturated acids dissolved in dry ether and cooled to -10°C bromine was added slowly until it was in slight excess During the process of bromination the temperature was not allowed to rise above -5°C The mixture was then allowed to stand at -10°C for two hours The hexabromide of linolenic acid that was precipitated was filtered off and washed with dry ether, dried and weighed The melting point of the hexabromide was found to be 176°C From the weight of the hexabromide and the knowledge of the percentage of bromine in it, the weight of linolenic acid was calculated and its percentage determined The ethereal solution consisting of the filtrate and washings from the above was treated with an aqueous solution of sodium thiosulphate in a separating funnel and the excess of bromine was thus removed The ethereal solution was then dehydrated with anhydrous sodium sulphate and the ether removed completely by distillation The residue was taken up with about 250 c c of dry petroleum ether, and the solution kept overnight in a refrigerator On standing, no precipitate was obtained showing the complete absence of linolenic acid hexabromide The petroleum ether solution was concentrated to about 50 c c by distillation and again kept in the refrigerator, but this time also no precipitate was obtained The petroleum ether was then completely distilled off, the residue weighed and its bromine content determined by the usual methods The percentage of bromine was found to be 36.4 thereby showing the complete absence of linolenic acid In fact the residue was completely oleic acid dibromide From this the weight of oleic acid was calculated The following table shows the results of the examination of the bromine addition products

TABLE IV
Examination of the Unsaturated Acids

Weight of the acids taken	15 0 gm
Weight of linolenic hexabromide	12 09 "
Percentage of bromine in the above	63 6 "
Melting point of the hexabromide	176°C
Weight of linolenic acid	4 56 gm
Weight of residue	16 4 "
Percentage of bromine in the above	36 4
Weight of oleic acid	10 4 gm.
Percentage of linolenic acid in the unsaturated acids	30 4
Percentage of linolenic acid in the mixed acids	26.1
Percentage of oleic acid in the unsaturated acids	69 3
Percentage of oleic acid in the mixed acids	59 4

The proportions of oleic and linolenic acids in the unsaturated acids were also determined from the iodine value of the mixture and they practically coincided with those found from the bromination products

Examination of the saturated acids—For the separation of the constituents, the mixed saturated acids were converted into their methyl esters by the usual methods, and the esters distilled under reduced pressure (6.5 mm.). Two main fractions (Nos. 1 and 2) distilling at 170–75° C and 175–80° C were obtained and from 17 gm. of the ester taken for distillation, the weight of the fractions were 11.02 and 5.6 gm. respectively. The following table shows the results obtained at a glance

TABLE V
Examination of the Saturated Acids

Fract. No.	I V	Mean M W	Palmitic acid		Stearic acid		Unsaturated acid	
			gm	%	gm	%	gm	%
1	3.4	271	10.1	90.4	0.2	1.6	0.3	2.3
2	21.9	292.1	1.1	20.0	3.38	59.6	0.86	15.4
		Total	11.2		3.58		1.16	

The percentage of various acids in the mixed saturated acids is given below

TABLE VI

Acid	Percentage in the saturated acids	Percentage in the mixed total acids
Palmitic	70.5	10.09
Stearic	22.6	3.23
Unsaturated	7.2	1.03

Examination of the unsaponifiable matter—The unsaponifiable matter obtained from the soap was found to be ordinary sitosterol, melting at 133–34° C. The acetyl derivative melted at 120° C.

Summary and Conclusions

The fixed oil from the seeds of *Lallelantia royleana* Benth. has been isolated in a yield of 10.8 per cent. by extraction with benzene.

Further examination of the oil revealed the presence of the following fatty acids

	%
Linolenic acid	26 1
Oleic acid	59 4
Palmitic acid	10 1
Stearic acid	3 2
Unsaponifiable matter (Sitosterol)	0 28

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SPECTROSCOPIC EXAMINATION OF THE DIFFRACTION OF LIGHT BY A THIN METALLIC HALF-PLANE

BY N ANANTHANARAYANAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

IN a previous paper the author (1939) has described and explained the features observed in the Fresnel diffraction by the edge of a thin film of silver bounded by a sharp edge. It was found that the position and visibility of the diffraction bands on the "shadow" side of the pattern varied in a remarkable manner both with the thickness of the film and the wave-length of the incident light. The sequence of changes described could be explained by considering the interferences between the plane wave transmitted by the film and the cylindrical wave radiated by the edge, the phase and intensity of the former being determined by the thickness of the film and the wave-length of the light. Since the optical properties of silver show marked changes with wave-length, particularly in the region of selective transmission, it was thought worth-while to study, in a systematic manner, the corresponding changes in the diffraction patterns. The use of the spectro-scope affords a simple and elegant method for such a study. It is known from the early observations of Stokes (1862) and from the extensive measurements of Minor (1903), that silver shows a characteristic variation in its optical constants in the vicinity of its sharp transmission band in the region of 3250 Å. This property of silver has been the subject of several interesting investigations [e.g., Rayleigh (1930), de Selincourt (1925), Wood (1934), etc.] It is to be expected, therefore, that a spectroscopic examination of the diffraction patterns due to thin silver films should exhibit interesting features. These have been investigated by the author in the present work.

2 Experimental Arrangements and Results

Silver films of the desired thicknesses terminating in sharp boundaries were prepared by the technique described in the earlier paper. Since the spectroscopic examination had to be made in the ultra-violet region, the metal was deposited on fused-quartz plates. With the edge of the film kept horizontal, the pattern formed in the light from a hydrogen-discharge tube with a quartz end-plate, was allowed to fall on the vertical slit of a quartz spectrograph such that the shadow of the film covered half the slit. The

portion of the pattern limited by the slit is spread out into a spectrum and the spectrograms show the variation in the intensity and disposition of the bands over the whole ultra-violet region where the spectrum of the hydrogen-discharge, as is well known, is continuous. The changes observed in the region of high selective transmission for silver lying in the vicinity of 3200 Å U are shown in Figs 1, 2 and 3 in Plate VI, for three different thicknesses of the film. Fig 1 corresponds to a very thin film which appeared pale brown in transmitted light. Fig 2 is due to a film which gave a blue transmission while Fig 3 is due to a thick film which was practically opaque to an incandescent filament.

Changes in the visibility of the fringes – The photographs of the diffraction patterns show several interesting features. It is found that, in all the three cases, the fringes on the ultra-violet side of the transmission band are fewer in number than in the visible spectrum. This is most clearly shown in the case of film No. 2 in which the pattern is well discernible on either side of the transmission band. As has been mentioned in a previous paper, the intensity of the transmitted light determines the “visibility” of the fringes, there being a large number of fringes of high visibility when the intensity of the transmitted light is sufficiently low. It is thus evident from the photographs, that the transmission of light by a silver film is more on the ultra-violet side of the transmission band than in the visible spectrum.

Considerable changes in the visibility of the fringes are noticed in the vicinity of the transmission band itself. In the case of the thinnest film the first dark fringe is that which is the best visible throughout the spectrum, indicating at the same time an increased visibility towards the ultra-violet end. The film of medium thickness shows a peculiar change in the visibility of the first dark fringe. On either side of the transmission band the fringes exhibit maximum visibility, in the region of transmission, however, the visibility is very low and the fringes are scarcely visible. Consequently, the pattern appears discontinuous in this region. This indicates that in the neighbourhood of 3200 Å U the intensity of the light transmitted by this film is so great when compared with that of the light diffracted by its edge that the destructive interference between the two is ineffective. The thickest film shows some features which are not exhibited by either of the two thinner films. In the first place, the first dark fringe happens to be the best on the ultra-violet side of the transmission band. As we approach the band, the visibility gradually falls off to a minimum at the transmission band. As we proceed farther towards the violet side, the visibility increases suddenly but again falls rapidly to such low values that the fringe is barely visible. The pattern, however, no longer appears discontinuous. The visibility of

the second dark fringe is found to be a maximum just where the first dark fringe has ceased to be clearly visible. These changes of visibility are a direct consequence of the feebleness of the transmitted light as well as its peculiar distribution in the spectrum, thus, a general idea of this distribution is obtained from an examination of the diffraction pattern.

Disposition of the bands—A remarkable feature exhibited by the photographs, is the sudden bend in the diffraction bands towards the "shadow" side of the pattern, when we pass from the visible to the ultra-violet region of the spectrum. This bend occurs at the region near 3200 Å, there being a point of inflexion almost at the transmission maximum. This effect is best shown by the first dark fringe. On the ultra-violet side of the transmission band the fringes appear to have been shifted away from the edge, showing thereby that in its transmission through the silver film the light has undergone a retardation of phase which takes place rather abruptly at the transmission maximum and continues to persist on the ultra-violet side. Though all the three films thus behave similarly, the extent of the phase changes described, depends on the thickness of the film. Thus with the thinnest film the bend and the shift of the bands are inconspicuous, so that, unless the first dark fringe is viewed along itself these effects cannot be readily observed. The film of medium thickness shows these features on a better scale. The phase retardation on the ultra-violet side of the transmission band is less than π as is shown by the fact that the first dark fringe on that side when produced falls just above the corresponding fringe on the other side. In the case of the thickest film both the effects have become all the more pronounced, the shift of the fringe on the ultra-violet side corresponding to a phase retardation of more than π .

3 Transmission of Light through a Metallic Film

As has been remarked before, the exact nature of the patterns depends upon the intensity and phase of the light transmitted by the film and the intensities and positions of the fringes can be worked out for a number of wave-lengths from the Fresnel integrals previously derived by the author (1939) for a metallic lamina. Such a detailed calculation, however, is unnecessary, since the general nature of the variation can be readily understood from the changes in phase and intensity of the transmitted light with wave-length. It has been shown before (author, 1939) that the complex amplitude of the transmitted light for a metallic film is given by the Drude-formula

$$C + iD = 2\mu_2/i(\mu_2^2 + 1) \sin m + 2\mu_2 \cos m,$$

where both μ_2 and m are complex, given by $\mu_2 = \mu(1 - ik)$ and

$$m = 2\pi\mu d/\lambda, (1 - ik),$$

μ , k being the optical constants of the metal for the particular wave-length λ of the incident light and ' d ' the thickness of the film. If the optical constants μ and k are known for various wave-lengths, the phases and intensities of the transmitted light are easily calculated. For very thin silver films (of the same order of thickness as film No. 1 in the present experiments) the optical constants are quite different from those of the metal in bulk if the classical theory were to explain the colour phenomena exhibited by them as they are gradually built up by sputtering or evaporation, as has been shown by Rouard (1937), moreover, since no accurate data are available for different wave-lengths, no calculations can be made for such films. For thicker films which show metallic lustre (e.g., films Nos. 2 and 3), however, the calculations can be done by assuming the optical constants to be the same as those of the metal in bulk, the effect of the substrate of quartz on which the films have been deposited being neglected for the sake of simplicity. Using the values of Minor (1903) for μ and $k\mu$ for silver over the range of wave-lengths 2930 Å U to 4500 Å U (see Table I), the phases

TABLE I

*Minor's values of μ and $k\mu$ for silver
for wave-lengths between 2930 Å U and 4500 Å U*

λ in Å.U	μ	$k\mu$
2930	1.568	0.969
3030	1.543	0.772
3090	1.485	0.598
3140	1.264	0.437
3180	1.015	0.431
3220	0.833	0.404
3260	0.689	0.424
3290	0.518	0.560
3320	0.404	0.649
3360	0.256	0.821
3460	0.219	1.098
3611	0.201	1.453
3950	0.155	1.912
4500	0.164	2.386

and intensities of the transmitted light for two silver films of thicknesses 5×10^{-6} cm and 10^{-5} cm respectively were calculated and curves have been drawn showing the variation of these factors with wave-length of the incident light. The curves are reproduced in Figs 1 and 2

It is seen from Fig 1 that the intensity of the transmitted light is a maximum at about 3250 Å U and falls off rapidly on either side. For the thinner film the rate of fall of intensity with wave-length towards the ultra-violet side is more rapid than that towards the visible region. For the thick film, though the general distribution of intensity remains the same, the rate of fall of intensity towards the violet side in the immediate neighbourhood of 3250 Å U. increases considerably, whereas that on the ultra-violet side is not so much affected. Moreover, the actual values of the intensity are much lower, with the result, the transmission band becomes highly localised in the spectrum. A comparison of the two intensity curves shows therefore, that the metallic absorption which extends from about 3250 Å U into the visible region and which is due to the conduction electrons in the metal, goes on increasing with the thickness of the film and becomes complete only when it is of the order of 10^{-5} cm; the edge of the absorptio_n

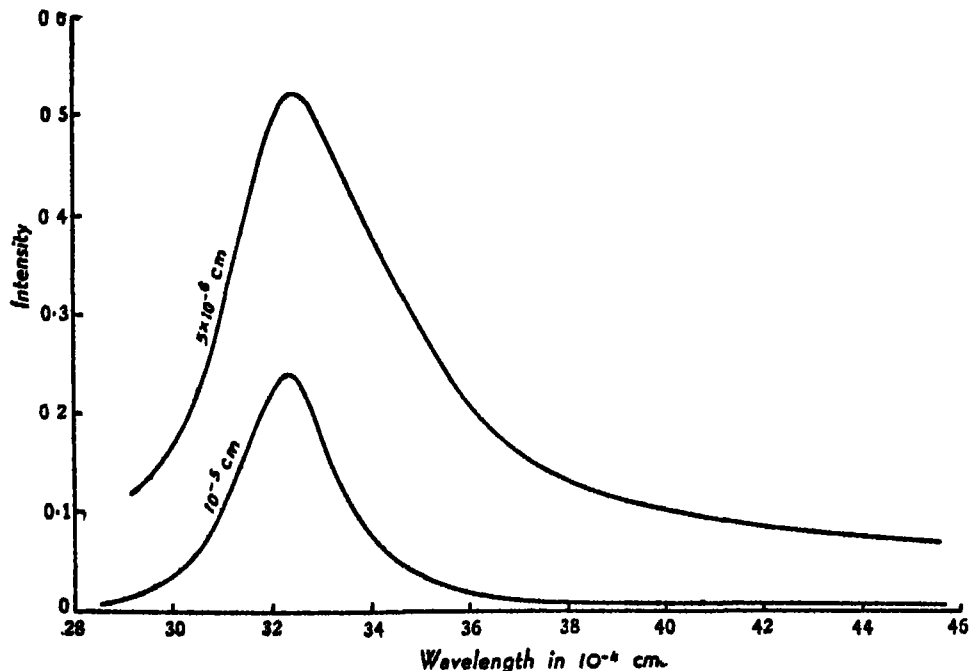


FIG. 1

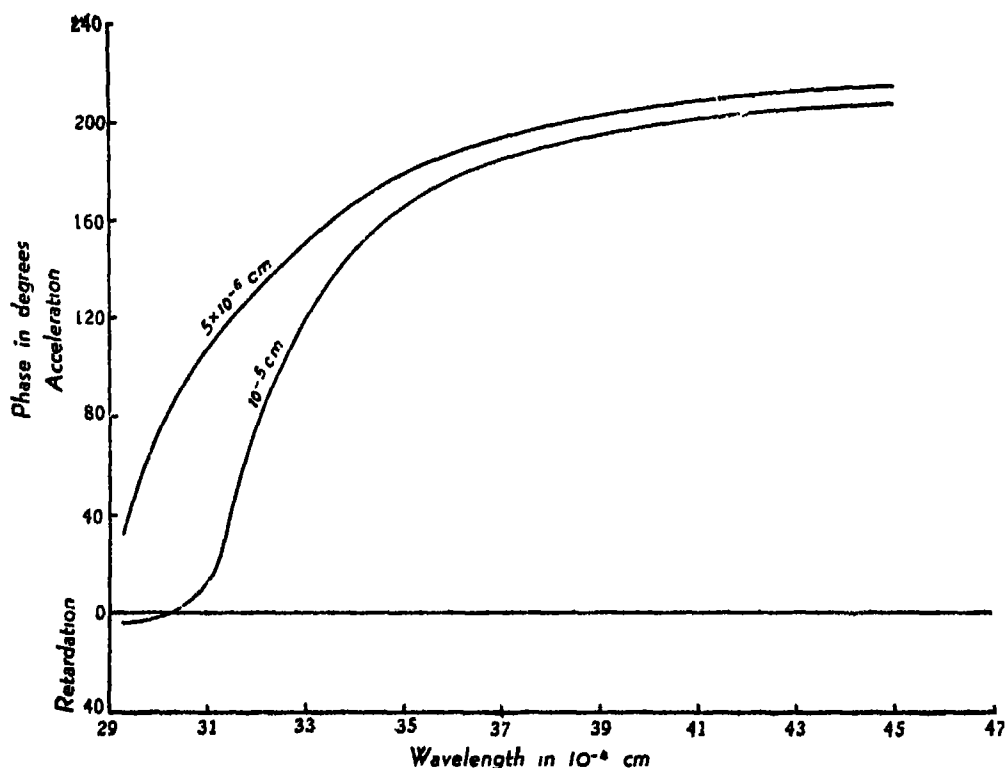


FIG 2

band due to the bound electrons, on the contrary, is less dependent on the thickness of the film. These points are well brought out in the photographs 2 and 3 in Plate VI, the absorption band on the visible side broadening towards 3250 A U more than the one on the ultra-violet side.

The phase curves (Fig 2) also show a similarity in their behaviour. For the thinner film the phase increases rapidly from low values at 3000 A.U. to π at about 3500 A U, the further increase in it being gradual even up to 4500 A U. For the thicker film the changes in phase are smaller than in the previous case throughout the range of 2930 to 4500 A U. At about 2980 A U the phase changes sign, showing thereby that upto a certain wave-length the waves are accelerated in the metal film.

4 Discussion

It has been pointed out in the preceding sections that the intensity of the transmitted light determines the visibility of the fringes while the phase determines their position. The effect of increasing the thickness of the film

therefore is to increase the general visibility of the pattern whereas the individual fringes themselves vary in their visibility at particular regions of the spectrum, depending upon the actual values of the intensity of the transmitted light in those regions. The changes of phase accompanying an increase in thickness of the film determine the disposition of the fringes in the spectrum. We have seen that the phase-changes at about 3200 Å.U. are abrupt and consequently the diffraction fringes in that region show a sudden bend. In the case of the thinner film (5×10^{-6} cm) the calculated curves indicate that the light waves are accelerated in the metal film even down to a wave-length of 2900 Å.U. In the case of the thicker film (10^{-5} cm) the actual values of the phase are smaller than those for the thinner film. This is explicable if we remember that the absorption due to the film goes on increasing with thickness till after a certain stage very little light is transmitted by the film. One may remark in general that after a thickness of 10^{-5} cm the metallic absorption is complete and the further increase in thickness would not sensibly alter the phase changes in transmission. We have also seen that for a sufficiently thick film, the waves are accelerated above a certain wave-length, whereas they are retarded in the ultra-violet. This is readily understood if we remember that for silver, as we recede into the ultra-violet, the refractive index of the metal is more than unity, whereas in the visible the refractive index becomes very small. The absorption index, however, is large wherever the refraction index is small and *vice versa*. The phase-changes in transmission, therefore, do not directly follow the refraction index curve, but are altered more or less by the absorption index. In the case of silver the refraction index equals unity at about 3200 Å.U., but the phase does not change sign at 3200 Å.U. as we have seen from the two curves. Even when the film is sufficiently thick, the effect of the absorption is to shift the position of zero phase farther into the ultra-violet (for 10^{-5} cm about 3000 Å.U.). For thinner films we have to recede more and more into the ultra-violet for this change of sign in the phase due to transmission.

Though the case of silver is unique in that it shows an extremely narrow transmission band, the cases of metals like Cu and Au are well worthy of study since these too show marked selective transmission.

In conclusion, the author desires to express his sincere thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

5 Summary

A spectroscopic examination of the Fresnel diffraction due to thin silver films bounded by a sharp edge reveals interesting changes in the visibility

and disposition of the bands in the spectrum. The visibility of the fringes is found to follow closely the spectral distribution of intensity of the transmitted light. At places where the intensity is sufficiently low, the first fringe ceases to be the best, the second fringe showing maximum visibility. These observations have already been recorded in a previous paper (1939). The fringes show a sudden bend with a point of inflexion in the region of selective transmission at 3200 Å U. and they are shifted away from the edge on the ultra-violet side and towards the edge on the visible side. Using the Drude-formula for the amplitude of the transmitted light and the experimental values of μ and $k\mu$ for silver, both the intensity and phase curves have been drawn for two films of thicknesses 5×10^{-6} cm and 10^{-5} cm respectively. The phase curves clearly explain the peculiar disposition of the bands at 3250 Å U.

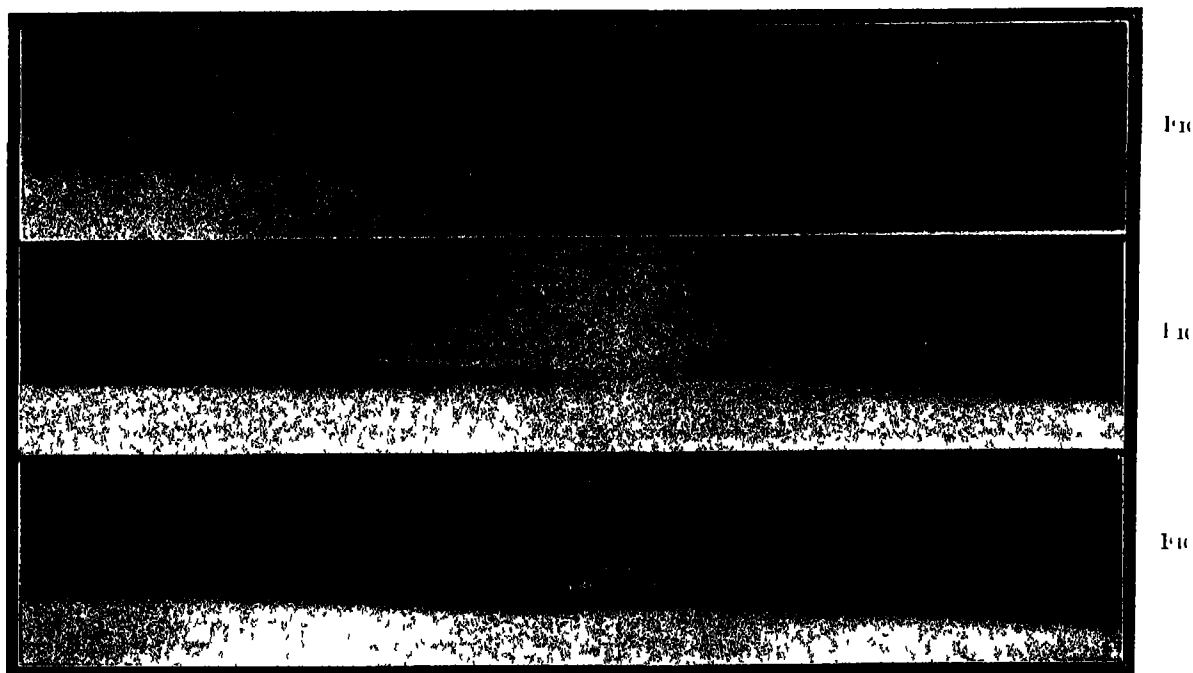
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4350

3200

2700



Spectrum analysis of the diffraction bands due to the edge of a thin silver film

A STUDY OF THE CHEMICAL COMPONENTS OF *DECALEPIS HAMILTONII* (MAKALI VERU)

Part IV. Resinols of *Decalepis Hamiltonii* and *Hemidesmus indicus*

By P BHASKARA RAMA MURTI AND T R SESHADRI

(From the Departments of Chemistry & Chemical Technology, Andhra University, Waltair)

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IN Part I¹ it was shown that the petroleum ether extract of the *Decalepis* roots contained a ketonic substance melting at 83°, resinol fractions melting between 130° and 185°, a definite compound of the same group melting at 235–36°, sterols and *para*-methoxysalicylaldehyde. The term resinol was used to indicate tentatively substances which were alcoholic in nature and which did not give the correct reactions of sterols and its use was justified by their similarity with substances of the type of amyryl. Their chemical composition approximated closely to the formula $C_{30}H_{50}O$. They gave a pink colour with Liebermann-Burchard reagent and a yellow solution with green fluorescence in Salkowski's reaction. Their exact nature has now been investigated.

As already described¹ the alcohol-soluble portion of the petroleum ether extract was separated into three fractions and from the middle fraction (B) melting at about 205–10° could be obtained after repeated crystallisations using ethyl acetate, besides fractions melting at 210–22°, a definite compound (M) melting at 235–36°. Further crystallisation of this compound from the same solvent raised the melting point to 239–40°. It has the formula $C_{32}H_{52}O_2$ and it is found to be an ester yielding on saponification acetic acid and a tri-terpene alcohol which has been identified as β -amyryl from a detailed study of its properties and the preparation of its derivatives. It therefore follows that the original substance (M) is β -amyryl acetate. Fractions melting between 210–22° could not be further purified but they had the same composition as (M). They were obviously mixtures of β -amyryl acetate with compounds of the same type which are isomeric with it.

The resinols were found to be present to a minor extent in the waxy portion and to a much higher degree in fraction (A) of the alcohol-soluble portion. The preliminary saponification and careful separation into various fractions of the unsaponifiable matter rendered identification of various components easy. By this means the sterols were effectively removed from

the resinols The separation and identification of the resinol mixtures have been carried out by the acetate as well as by the benzoate methods Fraction I melting at $175-85^{\circ}$ has been found to consist mostly of α -amyrin admixed with small amounts of β -amyrin The second fraction melting at $160-65^{\circ}$ contained lupeol as the main component and it was best isolated as the benzoate The amyrins were present only in small quantities

Fractions III, IV, V and VI melting at $155-57^{\circ}$ and below were individually examined Fraction III melting at $155-57^{\circ}$ contained β -amyrin and lupeol and very little of α -amyrin The other lower fractions (IV, V and VI) were very similar to it having the three above compounds in varying proportions Further in all of them were present small quantities of substances whose acetates were markedly more soluble in alcohol than those of the above resinols and which differed from them in giving a display of colours (pink-blue-green) with the Liebermann-Burchard reagent though they gave the same yellow colour with green fluorescence with the Salkowski's reagent Thus they exhibited characteristics, partly of sterols and partly of resinols They are being further investigated

Hemidesmus indicus —It was pointed out in Part III² that the composition of the petroleum ether extract of this root agrees closely with that of the *Decalepis* and that what Dutta, Ghosh and Chopra considered to be new sterols were really mixtures of resinols with small quantities of sterols This is now definitely supported by careful examination of the various resinol fractions The presence of lupeol and of α - and β -amyrins has been established. The compound melting at $235-36^{\circ}$ has been identified as β -amyrin-acetate During the careful examination of the various fractions, the special type of compounds mentioned in the case of the *Decalepis* as giving display of colours with the Liebermann-Burchard reagent and only yellow colour with Salkowski's reagent was also met with here Besides these a small quantity of a substance which is characterised by the yellow coloured solution having a brilliant green fluorescence which it gives with the Liebermann-Burchard reagent is obtained With the Salkowski's reagent it gives only an yellow colour This probably belongs to the tetracyclic triterpene type and this surmise gains support from the fact that on boiling with formic acid and benzene it undergoes transformation into a product of the pentacyclic type whose formation was indicated by the typical resinol colour reactions The yield however was very small and a detailed study could not be carried out so far

The results so far obtained may be summed up as follows : Though the two roots contained the same resinols the *Decalepis* has in it more of

amyrins than lupeol whereas in the case of the *Hemidesmus* roots the position is just the reverse

Experimental

Decalepis Hamiltonii Identification of β -amyrin acetate—The crystalline compound (M) melting at $235-36^{\circ}$ (0.5 g) was heated under reflux with 6% alcoholic potash (25 c.c.) for 5 hours and the contents were largely diluted with water. The crystalline precipitate that was formed was filtered and recrystallised from alcohol when it was obtained as needles melting at $196-97^{\circ}$. [Found C, 83.8, H, 11.2, $C_{30}H_{50}O$ requires C, 84.4, H, 11.7%] This was identified as β -amyrin by comparison with a sample described later on, the mixed melting point was undepressed. The filtrate was concentrated to a small bulk, acidified with dilute sulphuric acid and steam-distilled. In the distillate the presence of acetic acid was established by performing the lanthanum nitrate test carried out according to the procedure of Neelakantam and Row³. Hence the original compound (M) was identified as β -amyrin acetate. The melting point rose to $239-40^{\circ}$ after further crystallisation and it was unaffected by admixture with a sample of β -amyrin acetate whose detailed study is given later on in this paper. The results of combustion analysis have been given in Part I and they agree with the formula $C_{32}H_{52}O_2$.

As already described in Part I the resinols from (A) were fractionated into six fractions and the corresponding fractions from (W) were added to them, fraction I had m.p. $175-85^{\circ}$, II, $160-65^{\circ}$, III, $155-57^{\circ}$; IV, $151-53^{\circ}$, V, $135-45^{\circ}$ and fraction VI, $130-35^{\circ}$.

Resinol fraction I (m.p. $175-85^{\circ}$) Separation by the acetate method—The solid (2 g) was boiled with acetic anhydride (10 c.c.) and sodium acetate (4 g) for $2\frac{1}{2}$ hours and the mixture poured into water. After allowing it to stand for 12 hours the solid product was separated and crystallised from alcohol whereby a crop of crystals melting at 215° were obtained. Further repeated crystallisation from ethyl acetate raised the melting point to $222-23^{\circ}$ and at this stage the solid appeared as colourless shining elongated plates. [Found C, 81.6, H, 10.9, $C_{32}H_{52}O_2$ requires C, 82.1, H, 11.1%] $[\alpha]_D^{25}$, $+81.5^{\circ}$ in chloroform and that already recorded for α -amyrin acetate is $+83.0^{\circ}$.

The acetate was hydrolysed by heating with 5% alcoholic potash for 3 hours. After dilution with excess of water the resulting solid was crystallised from alcohol when glistening colourless needles melting at $185-87^{\circ}$ were obtained. [Found C, 84.0, H, 11.6, $C_{30}H_{50}O$ requires C, 84.4; H, 11.7%] $[\alpha]_D^{25}$ in benzene, $+92.1^{\circ}$ and the value noted by previous workers for α -amyrin $+93.3^{\circ}$. Thus the presence of α -amyrin in this fraction was established. This was further confirmed by the preparation of the benzoate

which melted at 192° (described later) The mother-liquor and washings from the crystallisation of the above-mentioned acetate were mixed and the solvent removed The solid residue thus obtained melted at $160-70^{\circ}$ It was first boiled with a small amount of methyl alcohol and filtered and subsequently recrystallised from ethyl acetate It now melted at $215-18^{\circ}$ and it could not be further purified by the ordinary methods [Found C, 81.9, H, 11.9, $C_{32}H_{52}O$ requires C, 82.1, H, 11.1%] On hydrolysis and purification of the resulting alcohol could be obtained a small quantity of β -amyrin melting at $196-97^{\circ}$ and a larger quantity of α -amyrin melting at $185-87^{\circ}$

Separation by benzoate method —The crystalline solid (2 g) was dissolved in dry benzene (20 c c) and treated in the cold with benzoyl chloride (10 c c) and pyridine (7 c c) The mixture was allowed to stand overnight and finally heated under reflux for 2 hours The contents were then diluted with water and extracted with excess of benzene The benzene solution was evaporated to dryness, the residue taken up in ether and shaken successively with aqueous sodium hydroxide, aqueous sulphuric acid and water On concentrating the ether solution and cooling in ice colourless needles of a solid melting at about 190° were obtained When further recrystallised from ligroin and benzene-alcohol mixture, the substance finally melted at $192-93^{\circ}$ [Found C, 83.6, H, 10.2, and $C_{37}H_{54}O_2$ requires C, 83.8, H, 10.2%] $[\alpha]_D^{25}$ in benzene, $+90.0^{\circ}$ and that recorded by previous workers for α -amyrin benzoate in benzene solution is $+87.3^{\circ}$ Further crops of the same substance could be obtained on concentrating the ether solution and recrystallising the solid from benzene-alcohol mixture The final fractions, however, melted at $165-75^{\circ}$ and no pure compound could be obtained from them The benzoate was hydrolysed by heating with 5% alcoholic potash for 5 hours By diluting the contents with a large excess of water and crystallising the resulting solid from alcohol, shining colourless needles melting at $185-87^{\circ}$ were obtained and these were found to be identical with the sample of α -amyrin obtained from the acetate method

From the results of analysis of the free alcohol, its acetate and benzoate and from their properties particularly specific rotations the presence of α -amyrin in fraction (I) as the predominant component is established β -Amyrin is present only in minor quantities.

Fraction II (m p $160-65^{\circ}$) —This solid (5.0 g) was dissolved in benzene (25 c c) and benzoyl chloride (15 c c) and pyridine (10 c c) added. The benzylation was effected just as before The crude benzoate mixture melted at 180° and when this was boiled with a small amount of methyl alcohol and filtered, the melting point rose to $210-20^{\circ}$ Subsequent crystallisation

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P 97, para 2, line 6 and p 98, para 4, line 15 read $[\alpha]_D^{25}$ in chloroform $+26.8^\circ$ and that recorded for lupeol in the literature $+26.4^\circ$, for 41.0 and 41.1 respectively

from ether yielded a compound melting at 249–54° Final recrystallisation (3 times) from ligroin yielded colourless gritty broad rectangular plates melting at 261–62° No change was effected by further crystallisation. [Found C, 83.4, H, 10.5, $C_{37}H_{54}O_2$ requires C, 83.8, H, 10.2%] $[\alpha]_D^{25}$, +62.5° in chloroform solution and $[\alpha]_D$ noted in the literature for lupeol benzoate, +60.9°

The benzoate was hydrolysed by heating with alcoholic potash for 5 hours according to the procedure already described The product was subjected to slow crystallisation from a mixture of alcohol and acetone By this means long needles, melting at 211–12°, were obtained Further crystallisation did not bring about any change [Found C, 84.0, H, 11.1, $C_{30}H_{50}O$ requires C, 84.4, H, 11.7%] $[\alpha]_D^{25}$ in chloroform, +41.0° and that recorded for lupeol, +41.2° From all the above results it is concluded that lupeol is present in this fraction

The mother-liquor and washings from lupeol benzoate were mixed and concentrated First crops of crystals melting at 240–50° were obtained which eventually yielded on purification lupeol benzoate Subsequent crops yielded on recrystallisation (4 times) from benzene-alcohol mixture a small quantity (0.2 g) of a solid melting at 231–32° [Found C, 84.2, H, 10.4, and $C_{37}H_{54}O_2$ requires C, 83.8, H, 10.2%] This benzoate on hydrolysis with alcoholic potash yielded a compound melting at 197–98° which was found to be identical with β -amyrin obtained from the acetate melting at 239° The mixed melting point was not lowered Hence the presence of a small quantity of β -amyrin in this fraction was established

The final mother from the above benzoates was evaporated to dryness and the residue dissolved in benzene-alcohol mixture and allowed to crystallise slowly After removing some indefinitely melting fractions α -amyrin benzoate melting at 192–93°, was obtained in well-defined needles and was found to be identical with the sample of the benzoate obtained from the first fraction The final residues yielded a solid melting at 140–70°

Hence fraction (II) contains lupeol as the main component mixed with α - and β -amyrins, the last being in the smallest quantity.

Fractions III, IV, V and VI—(Resinols melting between 130–57°) All these fractions gave very similar results. They were first acetylated and the acetates fractionally crystallised from alcohol A very small quantity of sparingly soluble fraction (1) melting at 235° was obtained After further crystallisation from ethyl acetate it was found to be β -amyrin acetate Subsequently several fractions (2) were collected from the alcohol solution One of these melted fairly sharp at 165–66° and on analysis yielded the following

results [Found C, 82.3, H, 10.6, and $C_{32}H_{52}O_2$ requires C, 82.1; H, 11.1%]

All these gave the pink colour with Liebermann-Burchard reagent and yellow colour with green fluorescence with Salkowski's reagent. The last and the most soluble fraction melted indefinitely at 120° and exhibited certain peculiar colour reactions. With the Liebermann-Burchard reagent it gave a play of colours pink-blue-green and with the Salkowski's reagent the sulphuric acid layer assumed orange yellow with green fluorescence on standing. These characteristics differ from those of well-known sterols and resinols and hence this fraction is being further examined.

The middle fraction of the acetates (2) given above could not be further satisfactorily separated into definite compounds. It was therefore hydrolysed and the free alcohols benzoylated. From this product, benzoates of lupeol, β -amyrin and α -amyrin could be obtained. Lupeol seemed to be the most important component in these fractions also.

Hemidesmus indicus — Fractions I (m.p. $175-85^\circ$), II (m.p. $165-70^\circ$), III (m.p. $155-65^\circ$) and IV (m.p. $150-54^\circ$) gave very similar results, hence they are reported together. First they were acetylated and the acetates fractionally crystallised from alcohol. The more sparingly soluble portion (A) melting at $190-200^\circ$ was repeatedly recrystallised from ethyl acetate when a very small quantity of β -amyrin acetate melting at 236° separated first. Subsequently the bulk of the acetate portion separated out melting at about 200° . After repeated recrystallisation (6 times) from ethyl acetate pure lupeol acetate (shining flat needles) melting at 214° was obtained from it. [Found C, 81.8; H, 10.4, $C_{32}H_{52}O_2$ requires C, 82.1, H, 11.1%] $[\alpha]_D^{25} + 45.4^\circ$ in chloroform solution and $[\alpha]_D$ for lupeol acetate is given in the literature as $+47.1^\circ$ in chloroform. The melting point was not depressed when mixed with lupeol acetate from *D. Hamiltonii*. When hydrolysed with alcoholic potash the acetate yielded a product which could be easily crystallised from alcohol. It was obtained as silky needles melting at 212° (Lupeol). $[\alpha]_D$ in chloroform solution is $+41.1^\circ$ and that recorded for lupeol is $+41.2^\circ$. Further no depression in the melting point was observed when mixed with the lupeol obtained from the *Decalepis* roots.

The alcohol mother-liquor from the crystallisation of acetates gave indefinite mixtures melting at $165-95^\circ$ and they were not further examined.

Fractions I and II were also benzoylated and the mixture of benzoates examined as in the case of *Decalepis Hamiltonii*. Pure lupeol benzoate was easily obtained from ligroin in a good yield from the first crop of crystals and the mother-liquor yielded indefinite mixtures melting at $180-220^\circ$. It was

therefore concluded that lupeol was the main component of these fractions and the amyrins probably occurred along with it. The presence of β -amyrin was definitely established

Fraction V (m p 135–40°) —This fraction was acetylated and the acetates were subjected to careful fractionation from an alcohol solution. It was noticed that the first fractions (m p 185–200°) gave the usual tests for the pentacyclic resinols, *i.e.*, a pink colour with the Liebermann-Burchard reagent and a yellow solution with the Salkowski's reagent. From the middle portions could be obtained a small quantity of a colourless solid melting at 135–45°. This behaved differently. With the Liebermann-Burchard reagent it gave a yellow solution with brilliant green fluorescence and the solution slowly assumed faint pink colour on standing. No test was given with Salkowski's reagent, only a very pale yellow solution being produced. This has been noted as the characteristic colour reaction of tetracyclic triterpenes and hence a sample of the substance was heated under reflux with a mixture of formic acid and benzene for 2 hours in order to bring about the formation of the pentacyclic triterpenes. After crystallisation from ethyl acetate the product melted at about 195° and it produced the usual pink colour with the Liebermann-Burchard reagent. Hence the existence of the tetracyclic compounds in the fraction V was indicated.

The final fractions of the acetates gave with the Liebermann-Burchard reagent a play of colours pink-blue-green but produced no red colour with Salkowski's reagent. These seem to be the same as the substances obtained in a similar manner from *Decalepis Hamiltonii*. The quantity was however too small to permit detailed study.

Summary

The existence of resinol in the petrol-soluble portions of *Decalepis Hamiltonii* and *Hemidesmus indicus* has been established by the isolation of α - and β -amyrins and lupeol from them. They exist both free and as esters. The various fractions have been analysed using both the acetate and the benzoate methods. The roots of the *Decalepis* contain more of the amyrins and less of lupeol whereas the *Hemidesmus* contains more of lupeol. The more soluble fractions of both roots seem to possess certain compounds having partly the properties of sterols and partly those of resinols. Further in *Hemidesmus* roots small amounts of tetracyclic triterpene alcohols also seem to be present.

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HETEROCYCLIC COMPOUNDS

Part XIV. Coumarins from 4-Ethyl-2-acetylresorcinol and β -Ketonic Esters

BY R D DESAI AND C K MAVANI

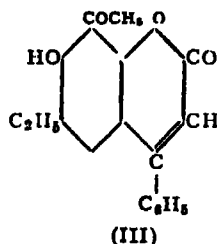
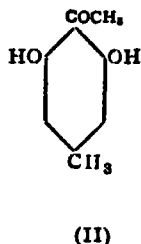
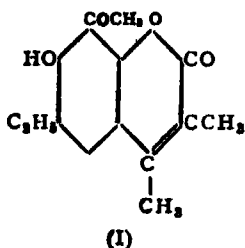
(From the Department of Chemistry, St Xavier's College, Bombay)

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It has been shown by Desai and co-workers¹ that resacetophenone as well as 5-ethyl-2,4-dihydroxy-acetophenone condense with aceto-acetic ester, not in the presence of concentrated sulphuric acid, but phosphoryl chloride with the formation of 7-hydroxy-coumarin derivatives. Limaye and Shenolikar,² on the other hand, have found that 2-acetylresorcinol undergoes the usual coumarin condensation in the presence of concentrated sulphuric acid. Desai and Ekhlās³ who happened to synthesise 4-ethyl-2-acetylresorcinol in course of some other work observed that it resembled 2-acetylresorcinol in its capacity for coumarin condensation in the presence of concentrated sulphuric acid. To make sure that this was not an isolated case, we have now condensed 4-ethyl-2-acetylresorcinol with C-alkylated aceto-acetic esters of the general formula $\text{CH}_3\text{-CO-CHR-COOEt}$, where R = methyl, ethyl, propyl, butyl and allyl groups. Thus methylaceto-acetic ester gave 3,4-dimethyl-6-ethyl-7-hydroxy-8-acetyl coumarin (I) while its higher homologues behaved in an analogous manner.

The constitution of the resulting coumarin was proved by its rational synthesis from 4-ethylresorcinol and methylaceto-acetic ester which gave 3,4-dimethyl-6-ethyl-7-hydroxycoumarin, the acetoxy derivative of which underwent Fries migration with the formation of 3,4-dimethyl-6-ethyl-7-hydroxy-8-acetylcoumarin. The constitution of other coumarins was similarly proved, and this proof is conclusive as Desai and Ekhlās¹ have shown that the Pechmann condensation of 4-ethylresorcinol and aceto-acetic ester gives exclusively 6-ethyl-7-hydroxy-4-methylcoumarin.

Desai and Miss Wakil⁴ have recently shown that 5-methyl-2-acetylresorcinol (II) undergoes de-acetylation during the course of the Pechmann Reaction. When this observation is compared with those recorded in this communication it becomes quite apparent how profoundly similar substituents situated in different places affect the course of the same reaction.



Finally 4-ethyl-2-acetylresorcinol was condensed with benzoyl acetic ester, when 4-phenyl-6-ethyl-7-hydroxy-8-acetylcoumarin (III) was obtained. The poor yield obtained in this reaction shows that this ester is less reactive than aceto-acetic ester.

Experimental

4-Ethyl-2-acetylresorcinol was prepared by Limaye's Process the details of which have been described by Desai and Ekhlas³ (*loc cit*). These have been recently repeated and confirmed by Limaye and Limaye⁵.

Condensation of 4-ethyl-2-acetylresorcinol with ethyl α-methylacetoacetate and formation of 3,4-dimethyl-6-ethyl-7-hydroxy-8-acetyl-coumarin—A clear solution of the dihydroxy ketone (2.5 g) and the ester (2 g) in 73 per cent sulphuric acid (25 c.c.) was kept at the room temperature for 36 hours, and poured over ice. The resulting solid crystallised from alcohol in colourless needles, m.p. 121° (yield - 75 per cent).

[Found C, 69.1, H, 6.2, $C_{18}H_{16}O_4$ requires C, 69.2, H, 6.2 per cent.]

The coumarin was easily soluble in chloroform, acetone, alcohol and acetic acid, sparingly soluble in benzene but almost insoluble in petroleum ether. Its alkaline solution was yellow and devoid of any fluorescence, and its alcoholic solution gave green colouration with alcoholic ferric chloride.

Condensation of 4-ethylresorcinol with ethyl α-methylacetoacetate and formation of 3,4-dimethyl-6-ethyl-7-hydroxycoumarin—A mixture of 4-ethylresorcinol (3 g), α-methylacetoacetic ester (3 g) and 73 per cent sulphuric acid (30 c.c.), after being kept for 12 hours was poured over ice. The solid crystallised from alcohol in colourless needles, m.p. 240° (yield = 90 per cent).

[Found C, 71.4, H, 6.55, $C_{18}H_{16}O_3$ requires C, 71.5, H, 6.5 per cent.]

It dissolved in alkali giving green fluorescence. The acetyl derivative prepared by heating the mixture of the coumarin (2 g), acetic anhydride (10 c.c.) and fused sodium acetate (2 g) for four hours crystallised from alcohol in lustrous needles, m.p. 150°.

[Found C, 69.0, H, 6.3; $C_{18}H_{16}O_4$ requires C, 69.2, H, 6.2 per cent.]

Fries Transformation of 3 4-dimethyl-6-ethyl-7-acetoxy-coumarin to 3 4-dimethyl-6-ethyl-7-hydroxy-8-acetylcoumarin—An intimate mixture of the acetoxy coumarin (1 g) and anhydrous aluminium chloride (2 g) was gradually heated in an oil-bath to 140° for one hour. The solid obtained by decomposing the excess of aluminium chloride with ice-cold hydrochloric acid was purified through alkali, and crystallised from alcohol when colourless needles, m p 121° , were obtained. Its m p was not depressed by the specimen prepared from 4-ethyl-2-acetylresorcinol and α -methylaceto-acetate.

Condensation of α -ethylaceto-acetate with 4-ethyl-2-acetylresorcinol and formation of 3 6-diethyl-4-methyl-7-hydroxy-8-acetylcoumarin—This was carried out as above. The Coumarin which was obtained in 70 per cent yield crystallised from alcohol in colourless needles, m p 147° . Its alkaline solution was yellow and non-fluorescent, while its alcoholic solution gave green colouration with alcoholic ferric chloride.

[Found C, 69.8, H, 6.8, $C_{18}H_{18}O_4$ requires C, 70.0, H, 6.8 per cent]

3 6-Diethyl-4-methyl-7-hydroxycoumarin was obtained by the usual method by condensing 4-ethylresorcinol with α -ethylaceto-acetic ester, and crystallised from alcohol in needles, m p 216° , (yield – 75 per cent). Its alkaline solution was yellowish and gave green fluorescence.

[Found C, 72.2, H, 7.0, $C_{18}H_{18}O_4$ requires C, 72.4, H, 7.1 per cent]

The Acetyl Derivative crystallised from alcohol in lustrous needles, m p 131° .

[Found C, 70.1, H, 6.8, $C_{18}H_{18}O_4$ requires C, 70.0; H, 6.6 per cent]

When subjected to the Fries Transformation in the usual manner, the above acetyl-derivative gave 3 6-diethyl-4-methyl-7-hydroxy-8-acetylcoumarin, m p 147° , and undepressed by the sample prepared from 4-ethyl-2-acetyl-resorcinol and α -ethylaceto-acetic ester.

Condensation of α -propyl-acetoacetate with 4-ethyl-2-acetylresorcinol and formation of 3-propyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin—This coumarin (70 per cent yield) crystallised from alcohol in colourless needles, m p 129° , and had the usual properties of its analogues.

[Found C, 70.6, H, 7.2, $C_{17}H_{18}O_4$ requires C, 70.8, H, 7.0 per cent]

3-Propyl-4-methyl-6-ethyl-7-hydroxy-coumarin obtained from 4-ethyl-resorcinol and α -propylaceto-acetic ester (65 per cent yield) crystallised from alcohol in yellowish needles, m p 189° .

[Found C, 72.9, H, 7.5, $C_{18}H_{18}O_3$ requires C, 73.1, H, 7.4 per cent]

The Acetyl Derivative crystallised from alcohol in needles, m p 133°

[Found C, 70.6, H, 7.2, $C_{17}H_{20}O_4$ requires C, 70.9, H, 7.3 per cent]

When this was subjected to the Fries migration it gave the coumarin m p 129°, which was proved to be 3-propyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin

Condensation of 4-ethyl-2-acetylresorcinol with α -butylacetoacetate and formation of 3-butyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin — As the α -butylaceto-acetic ester was slightly contaminated with the original unsubstituted aceto-acetic ester, the crude coumarin was fractionally crystallised from alcohol. The first fraction, m p 135°, was identified as 4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin while the second fraction, m p 100-105°, when recrystallised from benzene, melted at 124°. Its alcoholic solution gave green colouration with ferric chloride, and was identified to be 3-Butyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin

[Found C, 71.2, H, 7.5, $C_{18}H_{22}O_4$ requires C, 71.5, H, 7.3 per cent]

The coumarin obtained by condensing 4-ethylresorcinol with α -butylacetoacetic ester was a mixture of 3-butyl-4-methyl-6-ethyl-7-hydroxycoumarin and 4-methyl-6-ethyl-7-hydroxycoumarin. The former was more soluble in warm benzene than the latter. The soluble fraction on recrystallisation from alcohol gave colourless needles, m p 159°

[Found C, 73.5, H, 7.9, $C_{18}H_{20}O_3$ requires C, 73.8, H, 7.8 per cent]

The Acetyl Derivative crystallised from alcohol in lustrous needles, m p 114°

[Found C, 71.3, H, 7.5, $C_{18}H_{22}O_4$ requires C, 71.5, H, 7.3 per cent]

When subjected to the Fries Transformation, it gave a product, m p 124°, identified by the mixed m p as 3-butyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin which has been described before

Condensation of α -allyl-aceto-acetic ester with 4-ethyl-2-acetylresorcinol and formation of 3-allyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin — This coumarin crystallised from alcohol in yellowish needles, m p 106° (yield = 50 per cent)

[Found C, 71.0, H, 6.5, $C_{17}H_{18}O_4$ requires C, 71.3, H, 6.4 per cent]

4-Ethylresorcinol condensed with α -allyl-aceto-acetic ester in the usual manner giving 3-allyl-4-methyl-6-ethyl-7-hydroxycoumarin which crystallised from alcohol in needles, m p 202° (yield = 45 per cent)

[Found C, 73.5, H, 6.4, $C_{18}H_{18}O_3$ requires C, 73.7, H, 6.6 per cent]

The Acetyl Derivative crystallised from alcohol in needles, m p 123°

[Found C, 71.1, H, 6.6, $C_{17}H_{18}O_4$ requires C, 71.3, H, 6.3 per cent]

The Fries migration of this acetyl derivative gave the coumarin, m p 106° and identified as 3-allyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin

Condensation of benzoylacetic ester with 4-ethyl-2-acetylresorcinol and formation of 4-phenyl-6-ethyl-7-hydroxy-8-acetylcoumarin—The condensation carried out as usual was worked up after 36 hours when the resulting coumarin crystallised from alcohol in lustrous, prismatic needles, m p 154° (yield = 180 per cent) Its alkaline solution was yellow and non-fluorescent while the alcoholic solution gave deep-violet colouration with alcoholic ferric chloride

[Found C, 73.8, H, 5.4, $C_{19}H_{18}O_4$ requires C, 74.0, H, 5.2 per cent]

4-Phenyl-6-ethyl-7-hydroxycoumarin, obtained from 4-ethylresorcinol and benzoylacetic ester, crystallised from alcohol in colourless lustrous needles, m p 232° (yield = 90 per cent) Its yellowish, alkaline solution gave green fluorescence

[Found C, 76.5, H, 5.5, $C_{17}H_{14}O_3$ requires C, 76.6, H, 5.3 per cent]

The Acetyl Derivative crystallised from alcohol in lustrous needles, m p 151°

[Found C, 73.7, H, 5.4, $C_{19}H_{18}O_4$ requires C, 74.0, H, 5.2 per cent]

When this acetyl derivative was subjected to the usual Fries migration, 4-phenyl-6-ethyl-7-hydroxy-8-acetylcoumarin, m p 154°, was obtained

We are thankful to Rev Father G Palacios, SJ, and Prof R N Bhagwat for their kind interest in this work

Summary

The condensation of 4-ethyl-2-acetylresorcinol with α -methyl, α -ethyl, α -propyl, α -butyl and α -allylaceto-acetic esters as well as benzoylacetic ester has shown that this ketone is much reactive as contrasted with resacetophenone, thus showing that the Pechmann Reaction is not hindered by negative groups in the γ -position of the resorcinol molecule. The constitution of each coumarin was established by its rational synthesis from 4-ethylresorcinol, acetylating the resulting coumarin, and subjecting it to the Fries migration

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COLOURING MATTER OF THE FLOWERS OF *HIBISCUS CANNABINUS* : CONSTITUTION OF CANNABISCETIN

By K NEELAKANTAM, P SURYAPRAKASA RAO
AND T R SESHADRI

(From the Department of Chemistry, Andhra University, Waltair)

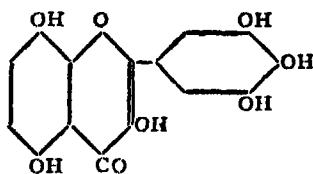
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HIBISCUS CANNABINUS (Deccan Hemp) is a small shrub cultivated in India for the sake of its valuable fibre and also as a vegetable. The flowers are light yellow in colour with a purple centre. A preliminary report of the chemical investigation of these flowers was made sometime back by Neelakantam and Seshadri¹ who announced the isolation of a new flavonol and its glucoside. They were named Cannabiscetin and Cannabiscitrin respectively because of their first isolation from the flowers of the cannabinus. Subsequently results have been obtained giving information regarding the constitution of the aglucone. A detailed account of the preparation and properties of the pigments and the determination of the constitution of cannabiscetin is given in this paper.

The dried petals were extracted with methylated spirit and the pigments isolated in various fractions according to the procedure already outlined in connection with other flowers.² The first fraction which was sparingly soluble in alcohol and came out on concentrating the alcoholic extract, consisted of the glucoside, cannabiscitrin. The aqueous solution subsequently obtained by diluting the alcoholic mother-liquor and removing the alcohol did not deposit any solid, but, when extracted with ether, yielded the aglucone, cannabiscetin. The neutral lead acetate fraction also seemed to consist mostly of the glucoside, which was, however, difficult to be purified. But pure cannabiscetin could be readily obtained therefrom after hydrolysis. The basic lead acetate fraction was too small to be studied. It could, therefore, be concluded that the colouring matter consists mostly of cannabiscitrin along with small quantities of the aglucone.

Cannabiscitrin has the formula $C_{21}H_{20}O_{13}$ and decomposes at about 245° . With alkaline buffer solutions, the substance yields two characteristic colorations—green and orange, the yellow colour that is first produced being evanescent. On acetylation it produces a colourless nonaacetyl derivative, and on hydrolysis with dilute sulphuric acid, it gives rise to glucose and the aglucone, cannabiscetin.

Cannabiscetin has the formula $C_{15}H_{10}O_8$ and does not melt below 350° . With ferric chloride, it gives a brown-black colour, and with dilute alkali, it undergoes a series of colour changes—yellow, green, blue, then olive green and finally light-brown. With alkaline buffer solutions the characteristic colorations are green, blue, crimson and purple, the initial yellow changing almost instantaneously, and these colour changes enable the flavonol to be easily distinguished from its glucoside. It yields a hexaacetyl derivative and a hexamethyl ether, thereby indicating the presence of six hydroxyl groups. It gives a deep red precipitate with neutral lead acetate solution, and undergoes decomposition with alkali and air, hence it should be a flavonol. It is isomeric with gossypetin, myricetin and quercetagenin. When treated with *p*-benzoquinone, it gives the "gossypetone" reaction just like gossypetin or herbacetin, thereby showing the presence of two hydroxyl groups in 5 and 8 positions. This is further supported by the rapid colour changes in alkaline buffer solutions just as in the case of gossypetin and herbacetin. As the result of oxidation in an alkaline solution exposed to air, it produces gallic acid which could be isolated and identified as its trimethyl ether. The completely methylated ether also yields trimethyl gallic acid, when boiled with 50% potash. These experiments prove the existence of hydroxyl groups in 3', 4' and 5' positions. Hence cannabiscetin may be represented as 3, 5, 8, 3', 4', 5'-hexahydroxy flavone.



Further details regarding the properties of cannabiscitrin and the position of the sugar group will be published later.

Experimental

Fraction 1—

Isolation of Cannabiscitrin—Dry petals of the flowers of *Hibiscus cannabinus* (2 kg) were extracted twice with methylated spirit, each extraction lasting for about 12 hours. The total alcoholic extract was concentrated to about 500 c.c. On leaving overnight a good amount of resin and wax separated out from the concentrate. They were removed by filtration through fluted filters. When the clear filtrate was allowed to stand for about 10 days, it deposited a large quantity of a yellow crystalline solid. It was filtered, and washed well with water till it assumed a pale yellow colour. It was then dissolved in pyridine and the solution diluted with water till the

impurities just began to separate out in a colloidal form. They were precipitated by adding a few drops of calcium chloride solution and then filtered. The clear filtrate which did not separate out any more impurities on further dilution, was concentrated on a water-bath till solid began to appear on the surface of the liquid. On leaving overnight, a good amount of a deep yellow crystalline substance separated. It was recrystallised from dilute pyridine, when it came down as rods and plates (25 g). It crystallised from dilute acetic acid as clusters of short yellow needles. On heating, it sintered at 210° fused at 220° , and decomposed at 245° . [Found in air-dried sample C, 46.7, H, 5.1, and loss on drying 10.0, $C_{21}H_{20}O_{13}$, 3 H_2O requires C, 47.2, H, 4.9, and loss (H_2O) on drying 10.1%.] [Found in the sample dried *in vacuo* at 110° C, 51.9; H, 4.3, $C_{21}H_{20}O_{13}$ requires C, 52.5, H, 4.2%.]

The glucoside was found to be easily soluble in alcohol, dilute and glacial acetic acids, and pyridine. When an aqueous alcoholic solution of the substance was treated with a drop of alkali, an olive-green colour was obtained; on adding more alkali, a pure yellow solution was produced. An alcoholic solution gave a reddish orange precipitate with neutral lead acetate, and with ferric chloride an olive-green colour which faded rapidly to dark-brown.

On boiling with acetic anhydride and anhydrous sodium acetate, the pigment yielded the nonacetate. It crystallised from glacial acetic acid (animal charcoal) as fine colourless needles. It was sparingly soluble in alcohol and even dilute acetic acid. A mixture of acetic anhydride and alcohol was found to be a convenient solvent for crystallisation. On heating it melted into a glassy mass at $200-02^{\circ}$ and did not flow down even at 260° . [Found C, 54.3, H, 4.4, $C_{21}H_{11}O_4$ ($OCOCH_3$)₉ requires C, 54.5, H, 4.4%.]

Hydrolysis of the Glucoside Preparation of Cannabiscetin—The glucoside (2 g) was hydrolysed by boiling with 7% sulphuric acid (50 c.c.). The solid went into solution on boiling for some time and within half an hour, the aglucone separated out giving rise to bumping. However the boiling was continued carefully over a mild flame for two hours. After cooling, the solid was filtered and crystallised from glacial acetic acid. It did not melt below 350° . When allowed to crystallise slowly, it came out as large yellow rectangular plates and prisms, but on rapid crystallisation it was obtained as flat needles and narrow plates. The yield was 1.2 g. [Found in air-dried specimen C, 53.7, H, 3.8, loss on drying 5.2%, $C_{18}H_{10}O_8$, H_2O requires C, 53.6, H, 3.6 and loss on drying (H_2O) 5.4%.] Found in the sample dried at 110° C, 56.4, H, 3.5, $C_{18}H_{10}O_8$ requires C, 56.6, H 3.1%.]

From the acid filtrate left after the removal of the aglucone, glucose was isolated in the form of its osazone by neutralising it with barium carbonate, concentrating it on a water-bath and subsequently treating it with phenyl hydrazine

Fraction II—

Cannabiscetin—The alcoholic mother-liquor remaining after the separation of the glucoside was concentrated to half its bulk and cooled. As no precipitate was thereby obtained, the solution was considerably diluted with water and the alcohol was removed almost completely on a water-bath. The resin that separated out during the course of this operation was carefully removed by decanting the liquid into a fluted filter. The clear filtrate was further concentrated and cooled. As no precipitate was obtained from this liquor even after several days, it was repeatedly extracted with ether. On distilling off the ether, a yellow crystalline solid was obtained (1 g). It was purified by crystallisation from dilute alcohol, when it appeared in the form of plates and prisms. The substance did not melt below 350°. It was identical in all its properties with cannabiscetin obtained from the new glucoside as already described. The identity was confirmed by preparing their acetyl derivatives and taking their mixed melting point.

Neutral Lead Acetate Fraction—The aqueous solution left after extraction with ether, did not deposit any solid on standing even for 15 days. It was then treated with neutral lead acetate solution, when an orange-red precipitate was obtained. From this lead salt the pigment was liberated by passing hydrogen sulphide repeatedly into its suspension in water. The precipitated lead sulphide was filtered off and the filtrate concentrated on a water-bath. But no solid separated out even after several days. Hence the calculated amount of concentrated sulphuric acid was added to make the solution 7% in the acid content and then boiled for two hours in order to hydrolyse any glucosides that might have been present. By this treatment a yellow crystalline substance was obtained (1 g). It was identified as cannabiscetin by comparison of the pigment and its acetyl derivative with authentic samples.

Properties of Cannabiscetin—The pigment was sparingly soluble in alcohol but it freely dissolved in glacial acetic acid and pyridine. It produced a deep red precipitate with lead acetate and a dark-brown colour with ferric chloride. It dissolved in very dilute alkali, producing at first a yellow solution which rapidly changed to green and then blue, gradually to olive-green and finally to light-brown.

Colour Reactions of the Aglucone and its Glucoside with Alkaline Buffer Solutions—Both the aglucone and the glucoside showed prominent colour

changes with alkaline buffer solutions of only high pH value, the following table summarises the changes

pH	Aglucone	Glucoside
8 0	Slowly dissolved to form a pale yellow solution which changed to yellowish brown after 24 hours	Dissolved slowly to a pale yellow solution which became yellowish red after 24 hours
8 6	The dissolution was more quick and the yellow solution acquired an orange tinge within an hour and became yellowish brown after 24 hours	Same changes as above but more rapid
9 2	Quickly dissolved, yielding a yellow solution, with a green tinge. The colour rapidly changed to yellowish green, then yellowish brown and to pure brown within 10 minutes. The brown became orange-red which was stable for an hour. The next day, it was still brown.	Same changes as above, but the final colour was orange-yellow (after 24 hours)
9 8	The initial yellow solution quickly turned to green and became within 5 minutes brown through dirty brown. It became orange-red within 10 minutes and remained so for an hour. After 24 hours it was brown.	Dissolved very quickly to produce a clear yellow solution which became orange after 24 hours
10 4	Quick succession of changes —yellow solution—bright emerald green—greenish-brown—brown—reddish brown—bright crimson (within 5 minutes). The crimson colour was stable for 1 hour and faded to brown the next day.	Quick succession of changes —yellow solution—yellowish green—again yellow. The solution slowly acquired an orange tinge and after 24 hours became definitely orange with a strong green fluorescence.
11 0	Same changes as above but more quick, the crimson appearing even within 2 minutes. Subsequent behaviour was also just the same.	Rapid changes —Yellow solution—greenish yellow—orange. It became brown after 24 hours.
11 6	The yellow solution changed rapidly to purple which gradually became reddish purple within an hour. It became brown as usual after 24 hours.	The yellow solution rapidly changed to green and became almost colourless within 10 minutes. After 24 hours it was brown.
12 2	Same changes as above, but the initial purple was mixed up with violet.	Same changes as above.
12 8	Very quick changes —yellow solution—emerald green—deep pure blue—purple—brown (within 5 minutes). The last colour faded quickly to pale yellowish-brown which was stable for 1 hour, and became dirty brown after 24 hours.	Same changes as above, but the tinge after 24 hours was green-brown.
13 4	Same changes as above, but the purple was less prominent.	Same changes as above, the green-brown giving place to faint brown.

Preparation of Hexaacetyl Cannabiscetin—The flavonol was acetylated by boiling with acetic anhydride and anhydrous sodium acetate. The acetyl

derivative was sparingly soluble in alcohol and freely in acetic anhydride. When crystallised from a mixture of acetic anhydride and alcohol, it came out as fine colourless needles sintering at 210° and melting at $214-15^{\circ}$. One more crystallisation from glacial acetic acid raised the melting point to $215-17^{\circ}$. [Found C, 56.6; H, 3.9, $C_{15}H_4O_2$ ($OCOCH_3$)₆ requires C, 56.8, H, 3.9%]

Preparation of Hexamethyl Cannabiscetin—(a) The flavonol (1.5 g) dissolved in methyl alcohol (30 c.c.) was treated with excess of methyl iodide (15 g) and refluxed on a water-bath. After sometime, methyl alcoholic potash (7 g of potash in 100 c.c. of methyl alcohol) was slowly added over a period of six hours. The solvent and the excess of the reagent were then distilled off, and water was added to the residue. After cooling, the alkaline liquid was just made acidic, when the ether separated out gradually as a sticky mass. It was purified through repeated crystallisations from alcohol using a little animal charcoal, and was obtained as colourless needles having the appearance of cotton wool.

(b) The pigment was also methylated through its acetyl derivative according to the method of Rao and Seshadri.³ Acetyl cannabiscetin (1 g) was dissolved in acetone (50 c.c.) and treated with dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.) alternately in small quantities, shaking vigorously after each addition. Finally the mixture was made strongly alkaline by the addition of 5 c.c. more of the alkali. The next day it was refluxed on a water-bath for an hour. The solvent was then driven off and the alkaline solution acidified with dilute hydrochloric acid, when the ether separated out. The solid was filtered and crystallised from dilute alcohol, using a little animal charcoal. The yield was 0.6 g.

The samples as obtained from the above two experiments were found to be identical and melted at $175-76^{\circ}$. [Found in the sample dried at 110° , C, 62.3, H, 5.4, OCH_3 , 46.1%, $C_{15}H_4O_2(OCH_3)_6$ requires C, 62.7, H, 5.5, OCH_3 , 46.3%]

Gossypetone Reaction with the Flavonol—The substance (0.5 g) was dissolved in absolute alcohol (8 c.c.) and *p*-benzoquinone (0.2 g) dissolved in a small amount of alcohol was added to the solution. A dull red crystalline substance began to separate out gradually. When the separation was complete, the solid was filtered and washed with a small quantity of absolute alcohol. [Found C, 56.8, H, 2.4, $C_{15}H_8O_2$ requires C, 57.0, H, 2.5%.] It had the appearance of red phosphorus. When treated with a drop of dilute alkali, it dissolved producing a blue solution which became red on acidification. On reduction with sulphurous acid, it gave back the original pigment.

Oxidation of the Flavonol Isolation of Trimethyl Gallic Acid—The flavonol (1 g.) was dissolved in 50% potassium hydroxide (15 c c) and left exposed to air for 24 hours with occasional stirring. It was then diluted until the strength of the alkali solution was about 20% and then treated with excess of dimethyl sulphate (15 c c) in small quantities. After some time, the excess of the methylating agent was decomposed by heating on the water-bath and the solution acidified with hydrochloric acid. The mixture looked brown and contained a good amount of resin. It was extracted with ether twice and the extract after evaporation left behind a brown viscous liquid which, on leaving in a refrigerator overnight, deposited a colourless crystalline solid. But the substance was still mixed up with a brown viscous resin, and the separation of the two by the ordinary methods of crystallisation was unsuccessful. The mixture was, therefore, pressed on a porous plate, when all the brown viscous liquid was absorbed by the plate, leaving free the colourless crystalline solid. It was scraped out and crystallised from water using a little animal charcoal. It was obtained as fine needles melting at 168–69°, and was found to be identical with the trimethyl ether of gallic acid.

Alkaline Hydrolysis of Hexamethyl Cannabiscetin—The methyl ether (0.5 g) was refluxed for 6 hours with 50% potash (20 c c) in a silver flask. At the end of this period, a major part of the solid was decomposed. The clear alkaline solution was diluted and then acidified with hydrochloric acid. On extraction with ether, the solution yielded a small amount of trimethyl gallic acid melting at 167–68°. The identification was confirmed by taking the mixed melting point with an authentic sample.

Summary

The colouring matter of the flower petals of *Hibiscus cannabinus* consists mostly of the glucoside cannabiscitrin along with small quantities of the corresponding aglucone cannabiscetin. The properties and reactions of these two substances are described along with those of some of their derivatives.

Cannabiscetin forms a hexaacetate and a hexamethyl ether. It is a flavonol exhibiting similarities with gossypetin and herbacetin particularly in regard to alkali colour reactions and gossypetone reaction. It yields gallic acid on being subjected to alkali fission, its methyl ether producing trimethyl gallic acid. It is, therefore, concluded to be 3, 5, 8, 3', 4', 5' hexahydroxy flavone.

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THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XIII. The Condensation of *o*-, *m*- and *p*- Chloro-benzaldehydes and of *m*-Bromo-benzaldehyde The Influence of Groups and Comparison with Perkin's Reaction

BY KANTILAL C PANDYA AND MISS RASHMI BALA PANDYA
(*The Chemistry Laboratory, St John's College, Agra*)

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PERKIN'S reaction was probably first used by him (1868) for the preparation of the valuable perfume coumarine. Although cinnamic acid had actually been prepared from benzaldehyde a little earlier, namely, by Bertagnini (1856) who had heated the aldehyde with sodium acetate and acetyl chloride in a sealed tube at 120–30°, and by Schiff (1870) who heated benzaldehyde with acetic acid and hydrochloric acid or zinc chloride in a sealed tube at 110–20°, and although controversies regarding the exact mechanism of Perkin's reaction started immediately, the method, with a little modification, soon became popular and attained a classical status in organic laboratory work (1877). It is still of very wide application.

The substitution of acetic acid by malonic acid was the next important step. Indeed it is interesting to realise that it was only in the course of the controversy about the mechanism of the reaction, going on between Perkin and Fittig, that the discovery was made by Stuart in Fittig's laboratory (1883), that the condensation of benzaldehyde to cinnamic acid took place equally well when sodium acetate was replaced by sodium malonate. Stuart also showed that instead of using acetic anhydride at 180°, if glacial acetic acid was used at 100°, better results were obtained. This method was then used by many workers, such as Komnenos (1883), Stuart, (1886), Fittig and Mackenzie (1894) and others. Satisfactory yields were also reported by Michael (1884) who merely heated the aldehyde with malonic acid alone in a sealed tube for several hours at 130–40°.

The next important change, so intimately associated with the name of Knoevenagel (1898), saw the introduction of a base, organic as well as inorganic, in place of acetic acid. His work was at first limited to aromatic aldehydes only (1896) but it soon extended to aliphatic aldehydes also (1902), and is now well known to travel far beyond this simple aldehyde-malonic acid condensation. The inorganic base was ammonia, in the form

of alcoholic ammonia or ammonium malonate or chloride. The organic bases were either the primary bases like aniline and ethylamine, or the secondary ones like diethylamine and piperidine, or piperidine hydrochloride. The inorganic and the primary organic bases were employed in full molecular or even larger proportions, but the secondary bases were employed in small proportions only. Piperidine in a few drops, the "Knoevenagel's Reagent" is now a very useful ally of the synthetic chemist (1894–1904).

It is remarkable that Knoevenagel did not find much use of pyridine or of any tertiary organic base. It was Verley, according to Boxer and Linstead, who used it first (1899), this use was extended widely by Doebner (1900 and onwards) and others. A very important observation is that of Harding and Weizmann (1910), who specially recommended the use of a tertiary base in cases like the preparation of nonylenic acid from heptaldehyde, where Perkin's method gave poor yields of a mixed product and where Knoevenagel's bases gave small yields invariably mixed up with other condensation products (such as those formed from the usual Schiff's condensation of aldehydes with bases). For this and similar condensations, pyridine was generally used in full molecular proportions, or even in greater excess. Staudinger advised the use of anhydrous pyridine in dry ethereal solution. Florence (1927) also recommended the same method for the synthesis of α - β unsaturated aliphatic acids.

The present-day practice in fact favours the combination of pyridine with piperidine, as first recommended by Robinson to Perkin (1924). Haworth, Perkin and Raukin (1924) did not obtain more than a 30% yield of 3,4-methylenedioxy-cinnamic acid from piperonal by Perkin's method, but found that, following Robinson's suggestion, the yield became 'almost quantitative' when piperonal, malonic acid and pyridine were taken in 1 : 2.5 : 6 mol proportions with a small amount of piperidine. [About ten years later, the same yield was obtained in this laboratory by Vahidy (1935) when the three were in the proportion of only 1 : 1.0 : 15 mol.] To-day the proportion of pyridine taken is about 3.5 mols for 1 of the aldehyde, according to the method established by Robinson and Shinoda (1925).

The fact that pyridine is also such an excellent solvent for so many substances and should therefore be used in liberal proportions to help the condensation on, and the other fact that as a tertiary base it is less active and strong than piperidine, and may be taken as inert, are probably responsible for the omission, in investigation as well as in literature, of the observation of the catalytic activity of pyridine. The earliest suggestion to this property seems to be contained in the interesting account of Bacharach and Brogan (1928),

who report that a few drops of pyridine used in Perkin's synthesis of cinnamic acid increased the yield to an optimum value of 85% (Had they used the pyridine alone, without the sodium acetate and acetic anhydride, they might have obtained the still higher yield of about 95%—*vide* Experimental) A little later, Boxer and Linstead (1931) found that 'Tertiary bases as such have a definite catalytic activity' A general and systematic study of this catalytic activity has still to be made

The work of Florence (1927) led Surange in this laboratory in 1929 to apply the pyridine method to a synthesis of aromatic α - β unsaturated acids When applied to aromatic aldehyde-malonic acid condensation, the original method had to be modified Nearly quantitative yields were obtained of the corresponding cinnamic acids from benzaldehyde and from *o*-, *m*- and *p*-nitro-benzaldehydes, when the aldehyde, malonic acid and dry pure pyridine were heated together without any solvent on the water-bath for a few hours Cinnamaldehyde also gave the same high yield, but of a mixture of cinnamylidene-malonic and phenylacrylic acids (unpublished) Surange's failure to obtain any condensation product from hydroxy-benzaldehydes seemed to have been shared by other workers, *viz*, Dutt, who had used an indefinite pyridine-piperidine mixture (1925)

The problem of the hydroxy-benzaldehydes was reinvestigated by Kurien and Pandya in 1931, who found that only a few drops of pyridine instead of one molecule, were able to do the work, and that in this way pyridine was as good a catalyst as piperidine or other tertiary bases (1934) The work has thereafter been pursued, and most of it published, (i) with a large number of aromatic aldehydes, (ii) with traces of other organic bases as well, most of which were tertiary, and (iii) with not only malonic acid, but also with malonic ester (occasionally) and with malonanilic acid (Mehra, 1938, 1939, Ittyerah, 1941, and Miss Pandya, unpublished) and with the three malon-*o*-, *m*- and *p*-toluidic acids (Ittyerah, unpublished), all of which contain the same reactive methylene group.

In all the above cases pyridine has been found to be a very efficient catalytic agent Other organic bases too show a similar ability in varying degrees, though one cannot say off-hand as to which base might give the maximum yield in a particular condensation Thus with salicylaldehyde, it was methylacridine that gave the highest yield (Khan and Kureim, 1935), with piperonal piperidine (Vahidy, 1935), with anisaldehyde isoquinoline (Vahidy, 1936), with *m*-hydroxybenzaldehyde pyridine (Vahidy, 1936), and so on

When no base and no other chemical agent is present and when the aldehyde and the acid are heated up alone, the condensation proceeds to take

place very slowly, the yield is very much smaller unless the heating is prolonged, and the condensation proceeds without the decarboxylation, the undecarboxylated product being isolable, under suitable conditions, in excellent yields and in a state of purity. In cases when on the aromatic ring the aldehyde has also other groups present, their nature and number have generally a very far-reaching influence on the whole reaction, particularly on its speed and on the yield.

This last point has already been made in an earlier paper by Pandya and Sodhi (1939). Recently Lock and Bayer (1939) have also made a study of the influence of groups on the yields obtained during Perkin's reaction under standardised conditions. A comparison can thus be made of the influence of groups in Perkin's reaction with the influence in the pyridine-trace condensation.

Under the conditions chosen, these workers obtain a yield of 49% of cinnamic acid from benzaldehyde. The influence of the halogen atom is stated to produce higher yields of the corresponding cinnamic acids, the position and the number of the halogens making an evident difference. Thus chlorine is stated to give the following yields, which are all higher than that given by the unsubstituted benzaldehyde, *i.e.*, higher than 49%.

Position of chlorine	2	3	4	2-3	2-5	2,6	2-3-6	nil
Yield %	71	63	52	62	78	82	66	49

That the yields are higher than those obtained from ordinary unsubstituted benzaldehyde is undoubtedly true, but no other generalisation regarding the influence of number and position would be safe as the figures are so irregular.

In the present paper the condensations of benzaldehyde, of the three chlorobenzaldehydes and of *m*-bromobenzaldehyde with malonic acid and with a trace of pyridine, as well as in the absence of any condensing agent, have been studied. In all the cases, the reactions go very well under the conditions described. Benzaldehyde with only four hours' heating on the water-bath, in the presence of a few drops of pyridine, gave a 95% yield of cinnamic acid. With the entree of a halogen, the reaction was very obviously quickened, so that in the case of the four haloid-benzaldehydes, the reaction was often completed in one hour, the yields were quantitative and the products, therefore, unusually pure. There is no doubt about the accelerating influence of chlorine and bromine here, nor any about this being the best of all the methods found in literature for the preparation of *o*-, *m*- and *p*-chloro- and *m*-bromocinnamic acids.

Originally all these four acids were first prepared by Gabriel (1882) and Gabriel and Herzberg (1883) by a roundabout process of preparing first

the desired nitrocinnamic acid, which was then reduced to the corresponding aminocinnamic acid, which was then diazotized to the diazonium nitrate or sulphate, and then this was warmed with fuming hydrogen chloride or with ten parts of strong hydrobromic acid. *o*-Chlorocinnamic acid was obtained a little later by Stuart (1888) from *o*-chloro-benzalmalonic acid, itself prepared by the 'Stuart-method' of heating *o*-chlorobenzaldehyde with malonic acid and glacial acetic acid. Perkin's method was first applied to *m*-bromobenzaldehyde by Miller and Rohde (1890) who, after heating the Perkin mixture at 140–50° for as many as twenty hours, obtained a 73% yield of *m*-bromocinnamic acid. Perkin's method was applied to the three chlorobenzaldehydes by Meyer and Beer (1913) and by Meyer, Beer and Lasch (1913), these have been confirmed by Lock and Bayer (1939) and have been stated above. Neither this nor any other group of workers has referred to the condensation of *m*-bromobenzaldehyde by Perkin's method under the standardised conditions, though they make a comparison of all the *p*-haloid-benzaldehydes, thus the yields of *p*-bromocinnamic acid from *p*-bromobenzaldehyde in two experiments (Perkin) are given as 48.6 and 52.6% respectively. This is about the same as their yield of the *p*-chlorocinnamic acid. Could we thus assume that the yield of the *m*-chlorocinnamic acid would be about the same as the yield of the *m*-bromocinnamic acid, their yield of the latter might then be about 63%. Against this, the yields of these four haloid-cinnamic acids obtained by our pyridine method range between 97 and 99%.

All the four haloid-benzaldehydes also condense with malonic acid when heated alone with them, giving, under carefully controlled conditions, nearly quantitative yields of the corresponding haloid-benzalidene-malonic acid. Of these only one, the *o*-chlorobenzalmalonic acid, has been previously described (Stuart, 1888).

The halogen undoubtedly increases the yield in the Perkin as well as in the pyridine-trace condensations, but the influence of the position of the halogen does not seem to coincide in both. The *p*-chlorine which seems to be most helpful in the pyridine-trace condensation appears to be the reverse in the Perkin condensation.

The three chlorobenzaldehydes undergo a similar condensation with malonanilic acid, but the details of this must find place in a separate paper.

Experimental

Condensation of Benzaldehyde

In the Presence of a Trace of Pyridine—1.06 g benzaldehyde, 1.04 g dry malonic acid and 0.13 g pyridine, purified in the usual way, (1.1 × 10⁻² mol) were heated together on water-bath for four hours, the mixture

soon became a homogeneous liquid and effervescence commenced within ten minutes of the heating and continued for about an hour. Cinnamic acid came out at the end in white crystals, which were extracted as usual and which then melted at 133° and weighed 1.4 g or 94.6% of theory. In another experiment the heating was stopped after two hours only, the yield was 1.3 g or 87.8%. This is considerably greater than that of Bayer and Lock, and is higher than the highest yield claimed under Perkin's method under the most favourable conditions.

Without any Condensing Agent — The same amounts of benzaldehyde and malonic acid were heated alone separately on water-bath in three different flasks that were heated respectively for four, six and eight hours. The mixture did not become a homogeneous liquid and no effervescence was observed. After about ten minutes a pinkish colour began to make its appearance and after one hour the whole mixture had become a pinkish solid mass. At the end of the heating, the benzalmalonic acid was extracted as usual by means of sodium carbonate and hydrochloric acid. It melted at 195–96° and weighed 1.5, 1.5 and 1.3 g respectively, the yield thus being 78, 78 and 73% respectively.

The Condensation of p-Chlorobenzaldehyde with Malonic Acid

(i) In the Presence of a Trace of Pyridine

The Materials — The *p*-chlorobenzaldehyde was very pure and melted at 47° (Literature gives 47°, 48°, 49°, Beilstein). The malonic acid, Merck, Pure for Scientific Purposes, was powdered, dried at 100° and kept in a desiccator. Pyridine, Extra Pure, Merck, or Purest, Schering-Kahlbaum, was kept over sticks of pure caustic potash for several days and fresh-distilled (b.p. 114–115°).

p-Chlorocinnamic Acid — 1.04 g malonic acid, 1.4 g *p*-chlorobenzaldehyde and 0.14 c.c. pyridine (1 : 1 : 0.16 mol proportions, 1/100th mol wt) were mixed in a flask and heated on water-bath without a condenser for four hours. The reaction started very quickly in two minutes the whole fused to a homogeneous liquid and effervescence commenced. In another five minutes, a cream-coloured solid mass made its appearance, and the whole mass had become perfectly solid long before the heating was stopped. It was allowed to cool, treated with 10% sodium carbonate solution and the small amount of the residue was removed by filtration. As the residue, however, gave the same high melting-point as the crude product, namely, 235°, it was clear that it was not the unreacted aldehyde, melting at 47°. In fact treatment with hot sodium carbonate solution dissolved it completely, and, on acidification of both the extracts, the same white precipitate was obtained.

On washing with water it melted at 245° . This must be highly pure as its melting-point, even before recrystallisation, was higher than that given in literature ($240-42^{\circ}$, Gabriel and Herzberg, *loc cit*)

The *p*-chlorocinnamic acid was a cream-coloured indistinct crystalline mass, very slightly soluble in water, alcohol, benzene, chloroform or carbon tetrachloride in the cold, slightly soluble in hot water or hot benzene, and soluble in acetone or in hot alcohol. Recrystallisation raised its melting-point to $246-47^{\circ}$, and it came out in long silky needles. It at once decolourized Baeyer's reagent. Yield 1.8 g (theoretical yield = 1.825 g)

In another experiment, the reaction mixture, of the same composition as above, was kept on the water-bath for only one hour instead of four, as the reaction seemed then to be complete. No aldehyde was recovered back, the *p*-chlorocinnamic acid was sufficiently pure, as, after a washing with water, it melted at $244-245^{\circ}$, and it was not necessary to extract it with sodium carbonate solution or to prepare the not very soluble sodium salt. The yield was again quantitative, and the melting-point, after recrystallisation, 247° (Lock and Bayer give the same)

(ii) *In the Absence of any Condensing Agent*

p-Chlorobenzalmalonic Acid —The aldehyde and the acid (1/100th mol) were heated alone, as before, on water-bath. The reaction was much slower, it required an hour's heating to change the whole to a clear liquid and there was no effervescence, even during eight hours' heating. Slowly a solid began to be formed and took several hours to be completed. The crude product was treated with cold 10% sodium carbonate solution which dissolved the whole and left no residue. Acidification with hydrochloric acid yielded a slightly cream-coloured solid, which was filtered and washed with cold water. The acid immediately decolourised Bayer's reagent, was very little soluble in cold water, moderately soluble in excess of hot water and easily soluble in alcohol or acetone even in the cold. Recrystallised from dilute alcohol, or dissolved in minimum quantity of alcohol and precipitated on scratching after the addition of a large amount of water, it came out in white needles, and after drying in the desiccator for 24 hours, it melted with effervescence at $197-98^{\circ}$. The yield was 1.8 g or about 80% of theory.

In a second experiment it was observed that the reaction was really completed in four hours and the yield then—2.25 g—was quantitative. Further confirmation of its identity was obtained from analysis (Cl, found, by Piria and Schiff's method 15.63%; $C_{10}H_7O_4Cl$ requires 15.67%. Equivalent weight by titration, found = 113.2 *p*-chlorobenzalmalonic acid requires 113.25. Molecular weight, silver salt, found 226.4; theory requires 226.5)

(iii) *Condensation with Ethyl Malonate*

3.2 g Ethyl malonate, Schering, Extra Pure, fresh redistilled, 2.8 g. *p*-chlorobenzaldehyde and 0.28 c.c. pyridine (1/50th mol, 1.1016) were mixed and heated together on water-bath for 26 hours. White needle crystals separated out of the liquid on cooling. They were filtered off from the mother-liquid, washed, dried on a porous plate, washed on the porous plate with a little water and dried. *m.p.* 235°. Insoluble in water and easily soluble in alcohol, the substance had the characteristic fragrant smell of esters. Yield 1.0 g (18% of theory). Recrystallised from alcohol, it melted at 237°. It instantly decolorised Baeyer's reagent (Cl, Found 12.09%, Ethyl *p*-chlorobenzylidenemalonate, $C_{14}H_{11}O_4Cl$ requires 12.56%)

The Condensation of m-Chlorobenzaldehyde with Malonic Acid

(i) *In the Presence of a Trace of Pyridine* —

m-Chlorocinnamic Acid—The aldehyde, the acid and pyridine were taken in the same proportion as above and heated on the water-bath. The reaction was slower distinctly than was observed with the *p*-isomer. It took ten minutes to liquefy completely and the effervescence continued much longer. In half an hour, the whole became solid again and the heating was stopped after one hour. The crude product was white and melted at 159°. It dissolved in sodium carbonate solution without leaving a residue, and *m*-chlorocinnamic acid was easily recovered on acidification of the sodium salt solution. After filtration and washing with water, it melted at 160°. It was readily soluble in cold acetone, soluble in alcohol and in hot benzene, less in hot water, still less in cold benzene. Recrystallised from alcohol repeatedly, the melting point remained stationary at 163°. Gabriel and Herzberg describe it as indistinct yellow, melting at 176°, which is not confirmed. Other workers, however, give the melting point at 165° (Heilbron, *Dictionary of Organic Chemistry*, 1, 276). It decolorised Baeyer's reagent. Yield 1.8 g (theoretical 1.825 g from 1.4 g of the aldehyde)

(ii) *Condensation without any Condensing Agent*

m-Chlorobenzylidenemalononic Acid—1.04 g Malonic acid and 1.4 g *m*-chlorobenzaldehyde were heated alone on the water-bath for four hours. A solid with a pale pink tint had been formed at the end, which dissolved completely in sodium carbonate solution, from this, on acidification, a cream-coloured solid was obtained which decolorised Baeyer's reagent, and which, on recrystallisation from alcohol, melted at 184–86°. It weighed 2.2 g (theoretical yield = 2.25 g) (Equivalent weight, found by titration with standard alkali, 113.6; the dibasic acid $C_{10}H_7O_4Cl$ requires 113.25 Cl, found: 15.29%; the chlorobenzylidene-malononic acid requires 15.67%)

*The Condensation of o-Chlorobenzaldehyde with Malonic Acid**(1) In the Presence of a Trace of Pyridine*

o-Chlorocinnamic Acid—The three were heated in the usual proportions on a water-bath. In ten minutes the reaction mixture became a clear liquid and effervescence started. Within half an hour a white solid began to be formed. After four hours' heating, the cold product was treated with a little cold water and a little ether. The remaining crude product melted at 207° and, when recrystallised from alcohol, melted at 210°. Further recrystallisations raised the melting point to 211–212°. The *o*-chlorocinnamic acid was then in the form of colourless needles. In literature Gabriel and Herzberg (1883) have described it as indistinct yellow, melting at 200°; Stoermer (1911) gives 205° as the m.p. and Lasch (1913) gives 211°. The yield was 1.8 g (the theoretical is 1.825 g).

Condensation without any Condensing Agent *o*-Chloro-benzalmalonic Acid—1.4 g *o*-chlorobenzaldehyde and 1.04 g malonic acid were heated alone on a water-bath for six hours. There was no effervescence, but the reacting mass began to solidify after only one hour's heating. The product was washed with water and dried. It melted at 185°, and, when crystallised from hot alcohol, it came out in white crystals, melting at 192°. Stuart also gives 192°. It weighed 2.1 g (93% of theory).

Condensation of m-Bromobenzaldehyde

In the Presence of Pyridine—0.925 g *m*-Bromobenzaldehyde, 0.52 g malonic acid and 0.07 g pyridine were heated together on a water-bath. The mixture immediately became a clear liquid and effervescence started within five minutes. Within half an hour a pale yellow solid began to come out in the liquid. In two concordant experiments, the total heating was two and four hours respectively. The solid dissolved completely in sodium carbonate solution, and the addition of concentrated hydrochloric acid drop by drop brought about the separation of white crystals of *m*-bromocinnamic acid. The yields were 1.0 and 1.1 g respectively, corresponding to 88.5 and 97% of the theoretical. The crude product melted at 170°, the recrystallised at 174°.

Condensation in the Absence of a Condensing Agent *m*-Bromobenzalmalonic Acid—1.04 g malonic acid and 1.85 g *m*-bromobenzaldehyde were heated alone on a water-bath in two separate flasks for four and eight hours respectively. The reacting mass did not liquefy nor effervesce, but in about 45 minutes a pale yellow solid began to emerge in view, till, as usual, the whole mass set as a solid. This was treated with cold sodium carbonate solution, the residual resinous matter filtered off and *m*-bromobenzalmalonic

acid precipitated as a white shining crystalline mass by careful treatment with strong hydrochloric acid. The acid was very soluble in cold alcohol and acetone, and was recrystallised from benzene or dilute alcohol or a benzene-alcohol mixture. It melted with effervescence at 192°. The yields were 2.4 and 2.7 g. or 87 and 99% of theory, respectively.

[Bromine found = 29.86% bromobenzalmalonic acid $C_{10}H_7O_4Br$ requires 29.52%. Equivalent weight found by titration = 135.4, required = 135.5]

Summary

1 Benzaldehyde and four haloid-benzaldehydes have been condensed with malonic acid, in the presence of a trace of pyridine as well as in the entire absence of any condensing agent.

2 The yields in all cases have been excellent, in some cases almost quantitative.

3 Chlorine and bromine have undoubtedly accelerated the condensation and increased the yields.

4 Compared to the yields obtained by Perkin's method, these yields are very superior, the condensations quicker and the products cleaner.

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A NOTE ON GLABRIN, A NEW COMPONENT OF THE SEEDS OF *PONGAMIA GLABRA*

BY N V SUBBA RAO AND J VEERABHADRA RAO

(From the Department of Chemical Technology, Andhra University, Waltair)

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IN a previous communication,¹ it was reported that by the extraction of the seed-cake of *Pongamia glabra* higher fatty acids along with some karanjin could be obtained. In our search for the presence of any further insecticidal principles, the cake was next subjected to extraction with alcohol and from this was obtained a small yield of a crystalline nitrogenous substance. Since its properties and reactions are not identical with any known compound, it is considered to be a new substance and it has been named Glabrin. It is best obtained from mature seeds since otherwise it has been noticed that the yield becomes practically negligible.

Glabrin melts at 290° with decomposition and has the empirical formula $C_7H_{14}NO_4$. It is very sparingly soluble in all the organic solvents. On the other hand it goes readily into solution in water. It is optically active and exhibits all the properties of α -amino acids of the dicarboxylic type, the most important being the ninhydrin test and copper salt formation. Attempts to determine the molecular weight have not been quite successful. However, titration with alkali without formalin and with the addition of formalin (Sorensen's titration) fixes the minimum molecular weight at 580 and consequently the molecular formula may be tentatively given as $C_{21}H_{42}N_3O_{12}$. Attempts to hydrolyse it using hydrochloric acid were not successful.

Since the yield of the substance is very low (0.1%), its extraction extremely slow and since it has no marked physiological properties, no further detailed work has been undertaken.

Experimental

The seed-cake of *Pongamia glabra* (3 kg) left behind after extraction of the seeds with petroleum ether was freed from the solvent and was subsequently extracted with methylated spirits in a continuous extraction apparatus. The process was very slow and therefore it was continued for 60 hours. The receiver containing the extract was set aside for a few days to complete the deposition of the crystalline solid that began to separate. It was then

filtered and washed with light petroleum. On careful examination it was found to be a mixture and that the components could be separated easily because of their differences in solubility in alcohol. The one that went easily into solution in hot alcohol was identical with karanjin in all its properties. The second which was sparingly soluble in all the common organic solvents could not be recrystallised in the normal manner, but, however, advantage was taken of its solubility in water. The substance (3 g) was dissolved in the minimum amount of water (10 c c) and then filtered so as to remove all the adhering impurities. The clear solution was then decolourised with vegetable carbon. Since attempts to obtain the substance in a pure condition, as for example by evaporating the aqueous solution, were unsuccessful, alcohol was added to the colourless aqueous solution in order to precipitate the substance. As the addition of alcohol did not bring about the separation of the substance, a large excess of ether was added to the aqueous alcoholic solution. Glabrin separated out as a shining colourless crystalline solid (rectangular plates). The mixture was allowed to remain overnight to facilitate the complete precipitation of the substance and was then filtered and air-dried.

Glabrin was found to melt with decomposition at 290° and contain nitrogen. [Found C, 47.8, H, 8.0, N, 8.0%, $C_7H_{14}NO_4$ requires C, 47.7, H, 8.0, N, 8.0%]. It went easily into solution in aqueous alkalis and acids. Further, its aqueous solution gave acidic reaction to phenolphthalein and litmus and produced effervescence with sodium carbonate and bicarbonate, indicating thereby the presence of one or more free carboxylic groups in the molecule. It exhibited optical activity and had a specific rotation, -56.1° .

When an aqueous solution of glabrin was boiled with alkali, no ammonia was evolved. Further, it did not produce any precipitate with Nessler's reagent. This eliminates the possibility of glabrin being an ammonium salt. However, it produced a deep blue colour when a pinch of copper carbonate was added to its aqueous solution and the resulting copper salt was found to crystallise in leaflets. It did not give the tests for an amino group. But on reduction with sodium and alcohol, it responded to the carbylamine reaction. In this connection it has been found that aspartic acid also does not directly give the carbylamine reaction. Glabrin gave a blue colour when boiled with ninhydrin. This is a test which all acids having a free amino group in the α -position to a free carboxylic group give. It is known that ninhydrin reaction is very sensitive in cases of amino acids and that ammonium salts also give a positive reaction provided the concentrations are sufficiently high. But the latter possibility has been ruled out as already described.

A solution of glabrin in water was titrated with standard alkali without and with the addition of formalin. The amount of alkali consumed in the latter titration was double that in the former. This clearly indicates the presence of one amino group and two carboxylic groups in the molecule. The calculated equivalent weight of the substance from the above data was 580.

Glabrin was subjected to acid hydrolysis using 20% hydrochloric acid with a view to obtain simpler products which could be more easily identified. But the resulting product was found to melt at the same temperature as glabrin and the mixed melting point of the substance was not depressed.

The toxic effect of glabrin on fish was studied by placing small fresh water fish in a solution of the substance in water (1 g in 1000 c.c.). As there was no perceptible change in the fish even after 24 hours, it was concluded that glabrin is non-toxic to fish.

The authors wish to express their gratitude to Prof. T. R. Seshadri for his interest and guidance throughout the work.

Summary

A new nitrogenous substance has been isolated from the seeds of *Pongamia glabra* and has been named Glabrin. Its composition and properties have been studied. It seems to belong to the group of complex amino acids and is non-toxic to fish.

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SYNTHETICAL EXPERIMENTS IN THE GROUP OF SYMPATHOMIMETICS—PART III

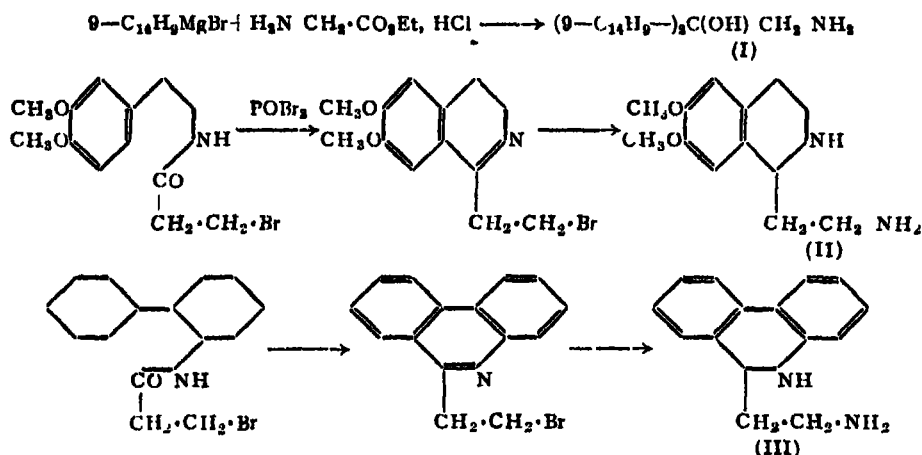
BY S RAJAGOPALAN

(From the Department of Pure and Applied Chemistry, Indian Institute of Science, Bangalore)

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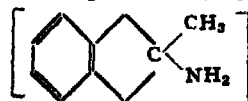
(Communicated by Sir C V Raman, KT, I R S, NI)

IN continuation of the study¹ on the relationship between chemical constitution and physiological activity of sympathomimetic amines derived from various ring-systems, one member of the group of β , β -bis-aryl- β -hydroxy ethylamines belonging to the phenanthrene series, *viz*, β , β -bis (9-phenanthryl)- β -hydroxy ethylamine (I), has now been synthesised in the usual way^{1,2} The present study also included the synthesis of a β -aminoethyl isoquinoline (II) and a β -aminoethyl phenanthridine (III) on the following lines



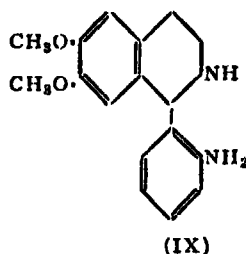
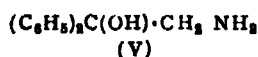
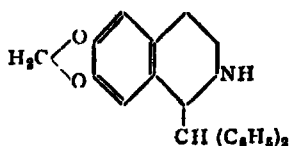
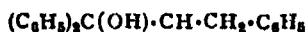
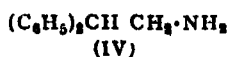
The scheme for the synthesis of compounds (II) and (III) had, however, to be ultimately abandoned owing to very low yields of the intermediate β -bromoethyl isoquinoline with the former and the failure of the cyclisation to 9- β -bromoethyl phenanthridine in the case of the latter

A survey of the literature on sympathomimetics brought to light the highly significant observation³ that methylaminohydrindene



is intensely active by virtue of its being doubly a β -phenyl ethylamine Based

on the above finding and actuated by considerations of the relative ease with which such bodies could be synthesised, the following compounds, possessing the requisite structure necessary for sympathomimetic activity, have been prepared



A close examination of the formulæ-picture of the compounds IV to VIII reveals the active groups, Ar C C N, being repeated in their molecules. The compound (IX), in addition to falling structurally in the class of the sympathomimetic norhydro hydrastinines, constitutes an interesting variation of a β -amino ethyl tetrahydro isoquinoline, wherein the α - and β -carbon atoms are linked by a double bond and form part of an aromatic nucleus.

A few of these compounds (IV, V and VI), although known in literature, were included for purposes of a comparative pharmacological study in progress elsewhere. β , β -Diphenyl ethylamine⁴ (IV) has advantageously been prepared now in good yields by the Hoffmann degradation of β , β -diphenyl propionamide⁵. The customary methods were adopted for the synthesis of the other members of the group.

The results of pharmacological examination of about twenty final compounds, hitherto synthesised, compared to tyramin as control, have been reserved for a future communication.

Experimental

β , β -Bis-(9-phenanthryl)- β -hydroxyethylamine (I) hydrochloride — A Grignard solution was prepared according to Bachmann⁶ from magnesium (3.54 g), 9-bromophenanthrene⁷ (38.3 g) and a mixture of ether (100 cc) and benzene (100 cc) in an atmosphere of dry nitrogen. Glycine ester hydrochloride (6.7 g) was added and the mixture refluxed for 1 hour on the water-bath, cooled, decomposed with dilute hydrochloric acid and the

separated solid filtered The hydrochloride was recrystallised once from alcohol-ether and once from dilute hydrochloric acid as almost colourless needles, m p 239–40° (dec) [Found Cl, 8 23, $C_{30}H_{24}ONCl$ requires Cl, 7 90%]

The *picrate* was obtained as greenish-yellow needles, m p 209–10° (dec) [Found N, 8 36, $C_{38}H_{28}O_8N_4$ requires N, 8 73%]

1-β-Bromoethyl-3 4-dihydro-6 7-dimethoxy isoquinoline

β-Bromopropionyl chloride — *β*-Bromopropionic acid⁸ (20 g) and thionyl chloride (18 c c) were heated together on the water-bath for 2 hours, and the reaction mixture fractionated The acid chloride was obtained as an almost colourless, lachrymatory oil, b p 115–17°/30 mm Yield 15 4 g

β-Bromopropionyl homoveratrylamide — A mixture of homoveratrylamine⁹ (5 g) and *β*-bromopropionyl chloride (5 g) in a little petrol was strongly cooled and gradually treated with dilute sodium carbonate under shaking The amide separated from water in long, colourless, prismatic needles, m p 120–21°; yield 2 5 g [Found N, 4 28; $C_{15}H_{18}O_3NBr$ requires N, 4 43%]

1-β-Bromoethyl-3 4-dihydro-6 7-dimethoxy isoquinoline — The above amide (2 4 g) in chloroform (20 c c) was allowed to react at the room temperature with phosphorus oxybromide (10 g) for 1 week with the exclusion of moisture The isoquinoline was obtained as a thick brown oil, yield, 0 4 g One half of the unreacted amide was recovered at the end of the experiment The *picrate* separated from acetic acid as a yellow powder, decomposing at 166–68° [Found N, 10 12, $C_{18}H_{18}O_3N_4Br$ requires N, 10 63%]

β-Bromopropionyl-o-amino-diphenyl, obtained in 50% yield, crystallised from alcohol in colourless needles, m p 118° [Found N, 4 80, $C_{18}H_{14}ONBr$ requires N, 4 83%]

β, β-Diphenyl ethylamine (IV) hydrochloride

*β, β-Diphenyl propionamide*⁵ — *β, β*-Diphenyl propionic acid¹⁰ (15 g) in chloroform (50 c c) was treated with thionyl chloride (10 c c), the mixture allowed to stand overnight and gradually added to well-cooled liquor ammonia (75 c c) containing a little sodium hydroxide (5 g) The amide, isolated in the usual way, was obtained in a yield of 12 g, m p. 124–25° [Found N, 6 34, $C_{18}H_{18}ON$ requires N, 6 22%]

β, β-Diphenyl ethylamine⁴ hydrochloride — The above amide (12 g) was shaken with a cold solution of sodium hypochlorite (from 4 g of potassium permanganate and 125 c c of 10% sodium hydroxide) The temperature was gradually raised to 65° and maintained at 65–70° for 1 hour, cooled, treated

with solid potassium hydroxide (45 g), heated at 70–80° for half-an-hour, cooled and thoroughly extracted with ether. The ethereal extract was washed and extracted with dilute hydrochloric acid. The aqueous acid solution was evaporated to dryness on the water-bath and the residual hydrochloride recrystallised from alcohol-ether in colourless needles, m p 256°, yield, 5 g [Found Cl, 14.94, $C_{14}H_{18}NCl$ requires Cl, 15.20%]

The *picrate* separated from alcohol as greenish-yellow crystals, m p. 210° (dec) [Found N, 13.10, $C_{20}H_{18}O_7N_4$ requires N, 13.14%]

β, β-Diphenyl-β-hydroxy-ethylamine (V) hydrochloride, prepared according to Thomas and Bettzieche² from phenyl magnesium bromide and glycine ester hydrochloride, crystallised from alcohol-ether in colourless needles, m p 191° (dec) [Found Cl, 13.85, $C_{14}H_{18}ONCl$ requires Cl, 14.23%]

The *picrate* separated from alcohol in yellow needles, m p 179° (dec) [Found N, 12.95, $C_{20}H_{18}O_8N_4$ requires N, 12.67%]

β, β-Diphenyl-β-hydroxy-α-benzyl ethylamine (VI) hydrochloride,² obtained by reaction of phenyl magnesium bromide (from 35 g of bromobenzene) and β-phenylalanine ester hydrochloride¹¹ (6 g) in fairly good yield (4.5 g), recrystallised from alcohol-ether as a white crystalline powder, m p 225–26° (dec)

Dibenzylaminomethane (VII) hydrochloride—The attempt to reduce dibenzyl ketoxime¹² with sodium amalgam to the desired amine was unsuccessful due, probably, to strong steric hindrance. The amine was, however, prepared by the modified Leuckart method¹³

Dibenzyl ketone (30 g) and formamide (20–25 c.c.) were heated together at 175–85° for 8 hours and, thereafter, worked up in the usual way

The *hydrochloride* recrystallised from dilute hydrochloric acid or alcohol-ether in colourless needles, m p 200–01°, yield 25 g [Found C, 72.14, H, 6.85, Cl, 14.20, $C_{18}H_{18}NCl$ requires C, 72.73, H, 7.27, Cl, 14.34%]

The *N-formyl-derivative* separated from alcohol in colourless needles, m p 88–89°, [Found N, 5.57, $C_{18}H_{17}ON$ requires N, 5.86%]

The *picrate* separated from alcohol in yellow plates, m p 191–92° (dec) [Found N, 12.59, $C_{21}H_{20}O_7N_4$ requires N, 12.70%]

1-Diphenylmethyl-1, 2, 3, 4-tetrahydro-6, 7-methylenedioxy isoquinoline (VIII) hydrochloride

Diphenylacetyl homopiperonylamide—Homopiperonyl amine¹⁴ (3.3 g) and a solution of the crude diphenyl acetyl chloride (from 4.5 g. of the acid and excess of thionyl chloride) in petroleum-ether were condensed together

in the presence of dilute alkali. The separated amide was filtered and recrystallised from alcohol in long, colourless needles, m p 139–40°, yield, 2.6 g [Found N, 3.84, $C_{23}H_{21}O_3N$ requires N, 3.90%]

1-Diphenylmethyl-3,4-dihydro-6,7-methylenedioxy isoquinoline—A mixture of the above amide (2.5 g), phosphorus oxychloride (7.5 c.c.) and dry toluene (20 c.c.) was gently refluxed on the sand-bath for 1½ hours with the exclusion of the moisture, cooled and poured on to crushed ice with stirring. The solution, after freeing from non-basic impurities by extraction with ether, was cooled in ice, basified with excess of sodium hydroxide and the separated solid filtered. The dihydro isoquinoline recrystallised from alcohol in colourless needles, m p 125–26°, after sintering at 120°, yield, 2.2 g [Found N, 4.01, $C_{23}H_{19}O_2N$ requires N, 4.11%]

1-Diphenylmethyl-1,2,3,4-tetrahydro-6,7-methylenedioxy isoquinoline hydrochloride—The crude dihydro base (2 g), zinc dust (10 g) and dilute sulphuric acid (60 c.c. of 1:4) were heated together on the boiling water-bath for 4 hours, filtered, cooled, basified with a large excess of ammonia and extracted with ether. The isoquinoline was purified twice through a dilute hydrochloric acid solution and the hydrochloride, obtained by evaporation of a dilute acid solution, crystallised from alcohol-ether in faintly yellowish, prismatic needles, m p 239° (dec), yield 1.6 g [Found Cl, 10.10, $C_{23}H_{23}O_2NCl$ requires Cl, 9.34%]

The *N*-acetyl derivative separated from alcohol in colourless needles, m p 172° [Found C, 77.26, H, 5.43, $C_{26}H_{23}O_3N$ requires C, 77.91, H, 5.97%]

The *picrate* crystallised from dilute acetic acid in yellow needles, m p 212–13° (dec) [Found, N, 10.32, $C_{28}H_{24}O_9N$ requires N, 10.15%]

1-(*o*-Amino)-phenyl-1,2,3,4-tetrahydro-6,7-dimethoxy isoquinoline (IX) hydrochloride

***o*-Nitrobenzoyl homoveratrylamide**—Homoveratryl amine (2.4 g) by condensation with *o*-nitrobenzoyl chloride in the usual way gave the crude amide (4.6 g, m p 138–40°). The amide crystallised from alcohol in colourless, silky needles, m p 142° [Found N, 8.44, $C_{17}H_{17}O_5N_2$ requires N, 8.51%]

1-(*o*-Nitro)-phenyl-3,4-dihydro-6,7-dimethoxy isoquinoline—The crude amide (4.5 g), phosphorous oxychloride (15 c.c.) and toluene (40 c.c.) were gently refluxed together for 1 hour and worked up as usual. The isoquinoline separated from alcohol in faint-yellow needles, m p 117°, after slight

shrinking at 112°, yield 4.2 g [Found N, 8.87, $C_{17}H_{15}O_4N_2$ requires N, 9.00%]

1-(*o*-Amino)-phenyl-1,2,3,4-tetrahydro-6,7-dimethoxy isoquinoline — The nitro dihydro base (1 g), zinc dust (10 g) and dilute sulphuric acid (60 cc of 1:4) were heated together on the boiling water-bath for 6 hours and worked up. The base separated from alcohol as hard, colourless crystals, m.p. 162° [Found C, 72.21, H, 6.36, $C_{17}H_{19}O_2N_2$ requires C, 72.07, H, 6.71%]

The monohydrochloride separated from alcohol-ether in clusters of colourless needles, m.p. 189° (dec.), after sintering at 183° [Found Cl, 11.50, $C_{17}H_{20}O_2N_2Cl$ requires Cl, 11.06, %]

The diacetyl derivative crystallised from alcohol as colourless needles, m.p. 196° [Found N, 7.42, $C_{21}H_{27}O_4N_2$ requires N, 7.63%]

Summary

With the object of studying the relationship between chemical constitution and physiological activity of sympathomimetically active amines, one member of the group $Ar_2C(OH)CH_2NH_2$, belonging to the phenanthrene series has been synthesised.

A number of simple bases derived from benzene and the isoquinoline ring-systems, possessing the requisite structure for sympathomimeticity, have also been prepared for purposes of a comparative pharmacological study.

The author's grateful thanks are due to Dr P. C. Guha for his interest in the work and to the Government of Madras for the award of a research scholarship.

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EINSTEIN SPACES ADMITTING THE LORENTZ GROUP*

BY MOHAMMAD SHABBAR

(From the Department of Mathematics, Muslim University, Aligarh)

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(Communicated by Dr M R Siddiqui)

I It was shown by Kosambi that the classical theories of relativity could be generalized by direct application of the Lorentz group to the trajectories. This gave rise to four-dimensional path-spaces, K_4

$$x^i - p^i \frac{Y}{X} G(\xi) + 2x^i \frac{Z}{X} \gamma(X, \xi) = 0, \quad (1)$$

($i = 0, 1, 2, 3$, γ arbitrary),

where Kosambi's notations are used †

$$g_{00} = -g_{11} = -g_{22} = -g_{33} = 1, \quad g_{ij} = 0 \quad i \neq j,$$

$$p^i = x^i, \quad p_i = g_{ij} p^j, \quad X = g_{ij} p^i p^j, \quad Y = g_{ij} x^i x^j,$$

$$Z = g_{ij} \dot{x}^i p^j, \quad \xi = \frac{Z^2}{XY}$$

It has also been shown by the same author in the form of a theorem that

The most general path equations derivable from three-dimensional observations and admitting the Lorentz group are

$$x^i - p^i \frac{Y}{X} G\left(X, \frac{Z^2}{Y}\right) + \dot{x}^i Z \gamma\left(X, \frac{Z^2}{Y}\right) = 0 \quad (2)$$

The purpose of this note is to discuss the conditions under which the most general Riemannian space, admitting the Lorentz group, can be an Einstein space when (i) the invariant R of the corresponding Ricci tensor survives, (ii) the invariant R vanishes

In what follows we shall consider an n -dimensional Riemannian space because it has been pointed out by Kosambi³ that if we extend our treatment to more than four-dimensions, with the corresponding extended Lorentz group, the results are valid also for n -dimensional space

* It is a great pleasure to me to thank Prof D D Kosambi for his kind suggestion and criticism during the course of this investigation. I have made free use of his unpublished manuscript entitled 'Path-equations admitting the Lorentz group II'.

† Besides these notations I use the universal notations as given in Eisenhart's "Riemannian geometry".

II The most general Riemannian metric, admitting the Lorentz group has the form

$$f = \frac{\alpha Y}{X} + \frac{\beta Z^2}{X^2} = \left(\frac{\alpha g_{ij}}{X} + \frac{\beta p_i p_j}{X^2} \right) x^i x^j, \quad (3)$$

α, β are functions of X ,

subject to the following conditions of non-degeneracy

$$\left| \frac{\alpha g_{ij}}{X} + \frac{\beta p_i p_j}{X^2} \right| = -\frac{\alpha^3 (\alpha + \beta)}{X^4} \neq 0^3 \quad (4)$$

If we put

$$\frac{\alpha'}{\alpha + \beta} - 1 = A, \quad \frac{2\alpha'\beta - \alpha\beta'}{\alpha(\alpha + \beta)} = B, \quad \frac{\alpha'}{\alpha} - 1 = C, \quad (5)$$

where *dash* indicates differentiation with respect to $\log X$, the geodesics of (3) are given by

$$x^i - p^i \left(\frac{\alpha Y}{X} + \frac{\beta Z^2}{X^2} \right) + 2C x^i \frac{Z}{X} = 0^3 \quad (6)$$

It is obvious that equations (6) are the particular cases of equations (1) and (2)

Taking $\bar{g}_{ij} = \frac{\alpha g_{ij}}{X} + \frac{\beta p_i p_j}{X^2}$

to be the fundamental metric tensor, we get the following invariants (the bar, put above, indicates that these invariants are derived from \bar{g}_{ij} , as the fundamental tensor)

$$\begin{aligned} \bar{R}'_{ijkl} = & \frac{U}{\alpha\gamma X} (\delta^i_l \bar{g}_{jk} - \delta^j_k \bar{g}_{il}) + \frac{S}{\alpha^2\gamma X^2} (\delta^i_k p_l p_j - \delta^j_l p_i p_k) \\ & + \frac{Q}{\alpha\gamma^2 X^2} (p^i p_l \bar{g}_{jk} - p^j p_k \bar{g}_{il}), \end{aligned} \quad (7, a)$$

$$\begin{aligned} \bar{R}_{ij,kl} = & \frac{U}{\gamma X^2} (g_{il} g_{jk} - g_{ik} g_{jl}) + \frac{Q}{\alpha\gamma X^3} (p_i p_l g_{jk} - p_j p_k g_{il}) \\ & + \frac{(\gamma - \alpha) U}{\alpha\gamma X^3} (p_i p_l g_{jk} - p_j p_k g_{il}) \\ & + \frac{S}{\alpha\gamma X^3} (g_{ik} p_l p_j - g_{il} p_j p_k), \end{aligned} \quad (7, b)$$

$$\bar{R}_{ij} = \frac{g_{ij}}{X} \left\{ (n-1) \frac{U}{\alpha\gamma} + \frac{Q}{\alpha\gamma^2} \right\} - \frac{p_i p_j}{X^2} \left\{ (n-1) \frac{S}{\alpha^2\gamma} + \frac{Q}{\alpha\gamma^2} \right\}, \quad (8, a)$$

$$\bar{R}_i = \bar{g}_{ij} \left\{ (n-1) U\gamma + Q \right\} \frac{1}{\alpha^2\gamma^2} + p_i p_j \frac{(n-2)Q}{\alpha^2\gamma X^2}, \quad (8, b)$$

$$\bar{R} = (n-1) (nU\gamma + 2Q) \frac{1}{\alpha^2 \gamma^2}, \quad (9)$$

$$X^2 \bar{W}'_{,kl} = \frac{Q}{\alpha \gamma^2} \left\{ \frac{X}{n-1} (\delta'_{kl} g_{,l} - \delta'_{l,k} g_{,l}) + p^l (p_l g_{,k} - p_k g_{,l}) \right. \\ \left. + \frac{1}{n-1} (\delta'_{kl} p_l p_k - \delta'_{k,l} p_l p_l) \right\}, \quad (10)$$

$$C_{ijkl} = 0, \quad (11)$$

where,

$$\left. \begin{aligned} \alpha + \beta &= \gamma \\ U &= \alpha'^2 - \alpha \gamma \\ Q &= 2 \alpha'' \alpha \gamma - \alpha \alpha' \gamma' - 2 \alpha'^2 \gamma + \alpha \gamma^2 \\ S &= -2 \alpha'' \alpha \gamma + \alpha \alpha' \gamma' + \alpha \alpha'^2 - \alpha^2 \gamma + \alpha'^2 \gamma \end{aligned} \right\} \quad (12)$$

The vanishing of the conformal curvature tensor (11) gives us

THEOREM I *The Riemannian spaces, admitting the Lorentz group, can be mapped conformally on an S_n for $n \geq 4$*

This theorem indicates that a transformation of co-ordinates exists such that

$$\frac{\alpha Y}{X} + \frac{\beta Z^2}{X^2} \rightarrow \bar{Y} \psi(X) \quad (13)$$

Let such a transformation be given by

$$x^i = \phi(X) x'^i \quad (14)$$

$$\text{Then,} \quad \bar{Y} = \phi^2 Y + 4 Z^2 (\phi \phi' + \phi'^2 X) \quad (15)$$

In order that (13) be satisfied it is necessary and sufficient that

$$\frac{4 (\phi \phi' + \phi'^2 X)}{\phi^2} = \frac{\beta}{\alpha X}. \quad (16)$$

The equation (16), being of standard form, can be integrated

III An n -dimensional Einstein space is one for which

$$\bar{R}_{ij} = \frac{\bar{R}}{n} \bar{g}_{ij}. \quad (17)$$

Substituting the values of R_{ij} and \bar{R} , (17) becomes

$$\bar{g}_{ij} (2-n) \frac{Q}{4\alpha^2 \gamma^2} + p_i p_j (n-2) \frac{Q}{\alpha^2 \gamma X^2} = 0 \quad (18)$$

The necessary and sufficient condition that the metric (3) should satisfy equations (17) is that

$$Q = 0 \quad (19)$$

Whence,

$$\bar{W}'_{,kl} = 0 \quad (20)$$

The vanishing of the projective curvature tensor indicates also the isotropy of the space ⁴

This gives us

THEOREM II *Einstein spaces, admitting the Lorentz group, are projectively flat and hence isotropic*

In classical Riemannian geometry it has been shown by Schouten and Struik⁵ that 'an Einstein space, if conformal to a flat space, is isotropic'. But in the present case, under discussion, an Einstein space, admitting the Lorentz group, is isotropic as well as conformal to a flat space. Therefore Theorem II is a consequence of Theorem I, hence the result of Schouten Struik

Because the isotropic spaces of positive curvature are of class one⁶, we shall find the condition such that Einstein spaces, admitting the Lorentz group, can be of positive curvature

For $Q = 0$, the curvature tensor (7, b) takes the following form

$$\bar{R}_{ijkl} = -\frac{U}{a^2\gamma} (\bar{g}_{ik}\bar{g}_{jl} - \bar{g}_{il}\bar{g}_{jk}). \quad (21)$$

Putting (19) in the following form

$$U' - U \left(\frac{2a'}{a} + \frac{\gamma'}{\gamma} \right) = 0, \quad (22)$$

it follows on its integration that

$$\frac{U}{a^2\gamma} = \text{constant} = k^2 \text{ (say)}. \quad (23)$$

In order that the Einstein space, admitting the Lorentz group, be of constant positive curvature.

$$\left. \begin{aligned} -\frac{U}{a^2\gamma} &> 0 \\ \text{or, } a\gamma - a'^2 &> 0 \end{aligned} \right\} \quad (24)$$

Because of the physical interest, as will be shown in Sec IV, we have a result for the most interesting case $n = 4$

It is possible to represent a natural gravitational field in flat spaces of five dimensions, if and only if $a\gamma > a'^2$.

If we take

$$\bar{R} = (n-1) \frac{1}{a^2\gamma^2} (nU\gamma + 2Q) = 0, \quad (25)$$

equations (17) become

$$\bar{g}_{ij} \{ (n-1) U \gamma + Q \} \frac{1}{a^2 \gamma^2} + \frac{(n-2) Q}{a^2 \gamma X^2} p_i p_j = 0 \quad (26)$$

Now, the necessary and sufficient condition that the metric (3) should satisfy equations (17) is that

$$\left. \begin{aligned} (i) \quad Q &= 0, \\ (ii) \quad (n-1) U \gamma + Q &= 0 \end{aligned} \right\} \quad (27)$$

The equations (25, 27) are compatible and the common solution is given by

$$U \equiv a'^2 - a \gamma = 0, \quad (28)$$

which equivalent of a condition due to Kosambi³

Equation (28) makes $\bar{R}'_{,kl} = 0$, for in (7, a) Q and S can be put in the form of U and its derivative with respect to $\log X$. Therefore We have

THEOREM III *Einstein spaces, admitting the Lorentz group, are flat, if and only if $\bar{R} = 0$*

Further integration of (28) is not possible unless we assign definite values to γ

IV The results, obtained in the previous sections, hold good also for $n=4$. Therefore, in the following pages we shall consider their physical aspects.

A fundamental need in Milne's theory of the expanding universe is that $x' = c x^2$ be a solution of equations (6), which leads to the condition that

$$\left. \begin{aligned} A + B - 2C + 1^2 \\ i.e., \quad \gamma = \text{constant} \neq 0 \end{aligned} \right\} \quad (29)$$

Now, the equations (23, 28) can be integrated, their solutions being respectively

$$a = \frac{1}{2} m^2 X^{2b^2} + \frac{1}{8 k^4 m^2} X^{2bk} - \frac{1}{2 k^2}, \quad (30)$$

where m, k^2 are constants of integration and $\gamma = 4 b^2$

$$a = (a + b \log X)^2, \quad (31)$$

where a is constant of integration and $\gamma = 4 b^2$.

So far our investigation was limited to pure geometrical considerations without any application of the Einstein-field equations

$$\bar{R}_{ij} - \frac{1}{2} \bar{R} \bar{g}_{ij} = -8 \pi \bar{T}_{ij}, \quad (32)$$

when matter is present in the space. Equations (32) reduce to $\bar{R}_{ij} = 0$ when the space is empty and this case, which corresponds to Schwarzschild's

classical treatment, has been discussed in Sec III. It is to be noted that the Schwarzschild values of g_{ij} for empty space do not make the space flat, except at a very great distance from the centre of mass, but in the present case the vanishing of \bar{R}_{ij} along with $\bar{R}=0$ gives a flat space (Theorem III)

Substituting the values of \bar{R}_{ij} , R into (32) we get the field-equations as follows

$$\bar{g}_{ij} (-4 a'' a \gamma + a'^2 \gamma + 2 a a' \gamma' + a \gamma^2) \frac{1}{a^2 \gamma^2} + \frac{p_i p_j}{X^2} \frac{2}{a^2 \gamma} (2 a'' a \gamma - a a' \gamma' - 2 a'^2 \gamma + a \gamma^2) = -8 \pi \bar{T}_{ij} \quad (33)$$

But

$$\begin{aligned} \bar{T}_{ij} &= \epsilon \bar{\lambda}_i \bar{\lambda}_j - p \bar{g}_{ij} \\ &= \epsilon x_i x_j M - p g_{ij}^2 \end{aligned} \quad (34)$$

$$\text{where, } M = \frac{\left\{ \frac{a^2}{X^2} + \frac{2 a (\gamma - a)}{X^3} \frac{Z}{Y} \sqrt{\frac{X}{Y}} + \frac{(\gamma - a)^2 Z^2}{X^3 Y} \right\}}{\frac{a Y}{X} + (\gamma - a) \frac{Z^2}{X^2}} \quad (35)$$

$$p = \frac{1}{8 \pi a^2 \gamma^2} (-4 a'' a \gamma + 2 a a' \gamma' + a'^2 \gamma + a \gamma^2)$$

$$\epsilon = -\frac{1}{4 \pi a^2 \gamma X Y} (2 a'' a \gamma - a a' \gamma' - 2 a'^2 \gamma + a \gamma^2),$$

$$\text{for } p_i p_j = x_i x_j \frac{X^2}{Y} \quad (36)$$

$$\text{If } \epsilon = 0, p = \frac{3}{8 \pi a^2 \gamma} (a \gamma - a'^2)$$

Therefore, if density is zero, pressure is +ve, zero, -ve, according as

$$a \gamma > a'^2 \quad (37)$$

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STUDIES IN THE FRIEDEL-CRAFTS REACTION

Part V. The Effect of Polar Substituents on the Reactivity of Para-substituted Phenyl Succinic Anhydrides with Simple Aromatic Hydrocarbons

By M A WALI, A K KHALIL, R L BHATIA AND S S AHMAD

(From the Department of Chemistry, Muslim University, Aligarh)

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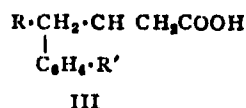
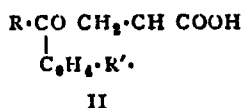
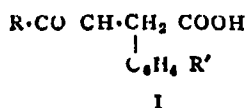
(Communicated by Dr M B Mirza)

IN the preceding communication,¹ evidence has been given to show that (a) the strong electron-donating character of the substituents, in the as-disubstituted succinic acids, is responsible for the total absence of isomerism, in condensations with simple aromatic hydrocarbons, (b) the tautomeric character of the phenyl group is the key-note for the appearance of isomerism in the condensation of phenyl succinic anhydride with simple aromatic hydrocarbons, (c) the presence of the solvent (Nitrobenzene), somehow, favours the formation of the α - β -substituted isomeride in preference to the β - β -substituted form, in the above phenyl succinic anhydride condensations, (d) the presence of the solvent (Nitrobenzene), somehow, inhibits the normal course of the reaction

In the light of the above observations, it is obvious that if the electron-attracting or the electron-repelling character of the phenyl group is strengthened by the introduction of positive or negative poles, as para-substituents in phenyl succinic acid, our surmise, that an increase in the proportion of β - β -substituted isomeride to that of the α - β -substituted form, corresponding to the electron-attracting capacity of the positive pole, would take place in the first case, and a decrease in the proportion of the same isomeride, corresponding to the electron-donating capacity of the negative poles, would take place in the other case, may not be untrue

The present investigation was undertaken, with a view, to gather as much experimental evidence as possible to lend support to our view-point. At the outset, we repeated the condensation of phenyl succinic anhydride with benzene in presence of nitrobenzene, as we considered it rather anomalous, that whereas, the anhydride condenses with toluene in presence of

nitrobenzene, and yields both the isomerides (*loc cit*), it does not condense with benzene under identical conditions² We were able to isolate, both the isomerides in the pure state in the proportion of about 11 : 89, largely in favour of α -phenyl- β -benzoyl propionic acid (II, where $R = C_6H_5$, and $R' = H$).



(Where $R = C_6H_5$ or C_7H_7 , and $R' = H, NO_2, CH_3, O$ or Cl)

The isomer in *m.p.* $154^\circ C$, gave the Piperonal and Pyrylium salt reactions, which further characterised its structure as α -phenyl- β -benzoyl propionic acid. Then we repeated the condensations of phenyl succinic anhydride with benzene, in absence of nitrobenzene (*loc cit*), and with toluene, with and without the solvent (*loc cit*) to get a more exact estimate of the mutual quantitative relationships of the two isomerides.

The work was extended to the condensation of (1) *p*-nitrophenyl and *p*-methoxyphenyl succinic anhydrides with benzene and toluene with and without the solvent (Nitrobenzene) and (2) *p*-chloro-phenyl succinic anhydride with benzene, under similar conditions. The experimental results obtained have been given under Tables I and II.

TABLE I

In the Absence of the Solvent (Nitrobenzene)

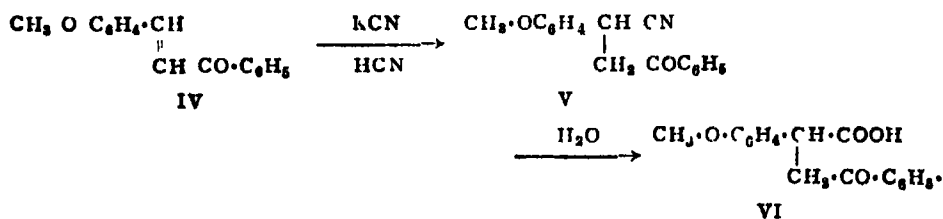
Substituent group in succinic acid	Condensed aromatic hydrocarbon	α - β -isomeride		β - β -isomeride	
		M.P. $^\circ C$	%	M.P. $^\circ C$	%
C_6H_5	C_6H_6	154	48	168	52
<i>p</i> -NO ₂ C_6H_4	"	167	45	185	55
<i>p</i> -CH ₃ OC ₆ H ₄	"	158	Preponderates		
<i>p</i> -ClC ₆ H ₄	"	146		166	54
C_6H_5	C_7H_8	150	23	154	77
<i>p</i> -NO ₂ C_6H_4	"	173	20	178	80
<i>p</i> -CH ₃ OC ₆ H ₄	"	147	82	158	18

TABLE II
In the Presence of the Solvent (Nitrobenzene)

Substituent group in succinic acid	Condensed aromatic hydrocarbon	α - β -isomeride		β - β -isomeride	
		M P °C	%	M P °C	%
C_6H_5	C_6H_6	154	89	168	11
p -NO ₂ C_6H_4	"	167	5	185	95
p -CH ₃ O C_6H_4	"	146	Preponderates	166	Preponderates
p -Cl C_6H_4	"				
C_6H_5	C_7H_8	150	83	154	17
p -NO ₂ C_6H_4	"	173	33	178	67
p -CH ₃ O C_6H_4	"	147	Preponderates		

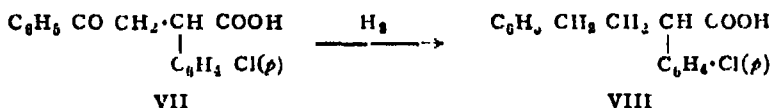
The α - β form of the keto-acids always gave the characteristic pyrylum salt reaction, with salicyl aldehyde in presence of hydrogen chloride, showing the presence of $-\text{CH}_2\text{C}=\text{O}$ grouping³ It also gave with piperonal, a pale yellow gum, invariably accompanied with piperonylic acid The β - β form, on the other hand, responded to neither tests indicating the absence of the unsubstituted methylene grouping

We were able to effect the rational synthesis of α - p -methoxyphenyl- β -benzoylpropionic acid (VI) from p -methoxy-chalkone (IV) and potassium cyanide according to the method of Lapworth and Hann⁴



We were also able to reduce β -phenyl- β - p -toluoyl propionic acid, m p 154° C (I, where $\text{R} = \text{C}_7\text{H}_7$, and $\text{R}' = \text{H}$) and β - p -chlorophenyl- β -benzoyl propionic acid, m p. 166° C (I, where $\text{R} = \text{C}_6\text{H}_5$ and $\text{R}' = \text{Cl}$) with its isomeride by Clemmensen's method and isolate β -phenyl- γ - p -tolyl butyric acid (III, where $\text{R} = \text{C}_7\text{H}_7$, and $\text{R}' = \text{H}$), γ -phenyl- β - p -chlorophenyl butyric acid

(III, where $R = C_6H_5$ and $R' = Cl$), and Y-phenyl- α -*p*-chlorophenyl butyric acid (VII and VIII)



Further researches in this direction are being carried on in these laboratories, and when the results of our investigations accumulate, we shall have a clearer insight as to whether our view-point, presented elsewhere, stands the rigour of the experimental tests or not. We are also busy in effecting the synthesis of the corresponding Naphthalene derivatives from the keto-acids, mentioned hitherto, in our work.

Experimental

(A) Condensations with phenyl succinic anhydride —

Condensation of phenyl succinic anhydride with benzene in nitrobenzene solution, and isolation of β -phenyl- β -benzoyl propionic and α -phenyl- β -benzoyl propionic acids — A solution of anhydrous aluminium chloride (10 gms) in nitrobenzene (50 cc) was gradually added to a mixture of the anhydride (5 gms) and dry benzene (15 cc) with constant shaking and cooling, and kept at the room temperature for 24 hours. It was decomposed with (dil) HCl, and then steam-distilled as usual. On cooling, a gum was obtained, which on purification through 10% sodium carbonate solution, and then drying, gave, on trituration with petroleum ether, a yellowish solid, m p 110–20° C (1.6 gms). On repeated crystallisation from benzene, it finally deposited white lustrous plates m p 154° C (0.32 gms) identified as α -phenyl- β -benzoyl propionic acid. The benzene mother liquor, finally, deposited a small amount of the isomer, β -phenyl- β -benzoyl propionic acid, m p 168° C (0.01 gm). The final mother liquors were dried, and on treatment with ethyl alcohol, yielded insoluble inorganic impurities (0.5 gm), and a further amount (0.04 gm) of the isomer, m p 168° C, on concentration. The residual sticky substance with benzene-hexane, gave the neutral substance, m p 285° C (0.05 gm) and then a yellowish gum, which on repeated treatment with hot water, gave a white solid, eventually melting at 164–67° C (0.4 gm), identified as impure phenyl succinic acid. While the keto-acid, m p 154° C gave with piperonal, a pale yellow gum, along with piperonylic acid, m p 226–27° C, the isomeric keto-acid, m p 168° C failed to respond the test and was always recovered unchanged. The former keto-acid gave also a pyrylium derivative, a crimson red powder, readily soluble in (dil) caustic soda solution, and not melting below 300° C.

Phenyl succinic anhydride (6 gms) and dry benzene (18 c c) were condensed in presence of anhydrous aluminium chloride (10 gms), and 0.6 gm of the keto-acid, m.p. 154°C , 0.65 gm of the isomer, m.p. 168°C , and 0.6 gm. of the neutral substance, m.p. 285°C were obtained

Then phenyl succinic anhydride (5 gms) was condensed, as usual, with dry toluene (15 c c) in presence of anhydrous AlCl_3 (8 gms), and 2.7 gms of the isomer, m.p. 154°C and 0.8 gm of the other isomer, m.p. 150°C were isolated. Under identical conditions the above experiment was repeated in presence of the solvent, nitrobenzene (50 c c), and the isolation of 0.2 gm of the β - β -isomeride, m.p. 154°C and 1.0 gm of the α - β -form was effected

(B) Condensations with *p*-nitrophenyl succinic anhydride —

p-Nitrophenyl succinic acid was prepared by direct nitration of phenyl succinic acid with (fuming) nitric acid at 0°C , according to the method of Fischter and Walter⁵. The crude solid, m.p. $200\text{--}10^{\circ}\text{C}$, when repeatedly crystallised from (dil) alcohol, yielded white shining needles, m.p. 218°C . The anhydride was obtained by heating the above acid (12 gms), with acetic anhydride (20 c c) for 4 hours and distilling excess of the acetic anhydride, under reduced pressure. The crude anhydride on crystallisation from ether, gave yellowish needles, m.p. 73°C (10 gms).

Condensation of p-nitrophenyl succinic anhydride with benzene and separation of β -p-nitrophenyl- β -benzoyl propionic and α -p-nitrophenyl- β -benzoyl propionic acids — The proportions used were redistilled dry benzene (36 c c), the anhydride (12 gms) and powdered anhydrous AlCl_3 (16 gms). The crude solid, m.p. $150\text{--}60^{\circ}\text{C}$ (8 gms), obtained after steam-distillation, was purified through 10% sodium carbonate, and gave a solid, m.p. $160\text{--}65^{\circ}\text{C}$ (7.4 gms). It was repeatedly extracted with hot benzene and finally left a residue, m.p. $170\text{--}76^{\circ}\text{C}$, ultimately raised to 185°C (0.6 gm) on re-crystallisation from methyl alcohol, and then hot benzene (long white needles). It was identified as β - β -substituted isomeride.

(Found. C, 64.7, H, 4.5, N, 4.8. $\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}$ requires C, 64.2, H, 4.3, N, 4.6%)

Concentration of the benzene extract, ultimately gave (a) a white crystalline solid, m.p. 218°C (0.6 gm) identified as the unchanged *p*-nitrophenyl succinic acid and (b) a white solid (small shining cubes), m.p. 167°C (0.5 gm) identified as α - β -substituted form, which gave the characteristic pyrylium and piperonylidene salt reactions.

(Found. C, 64.4, H, 4.8; N, 5.0. $\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}$ requires C, 64.2, H, 4.3; N, 4.6%)

On further concentration, the benzene mother liquor gave a solid, m p 120–30° C (0.3 gms), which foiled all attempts to resolve it into its components. Finally a brown sticky neutral substance (5 gms) was left behind, which could not be solidified.

Condensation of p-nitrophenyl succinic anhydride with benzene in nitrobenzene solution—The anhydride (10 gms) and dry benzene (30 c.c.) were condensed as usual, in presence of a solution of anhydrous AlCl_3 (12 gms) in nitrobenzene (50 c.c.). The solid obtained, on purification through sodium carbonate solution, melted at 170–85° C (5.4 gms), and from benzene-petrol, gave a white crystalline substance, m p 182–85° C. When re-crystallised from methyl alcohol, it gave small colourless needles, m p 185° C (1.0 gm) of β - β -substituted isomeride. The benzene extract, first deposited a crystalline substance, m p 218° C (1.0 gm), identified as the unchanged acid, and then a brownish solid, m p 175–80° C, which from methyl alcohol, yielded a further amount of the isomer, m p 185° C (1.0 gm). Further concentration of the benzene mother liquor, gave a solid, m p 150–60° C, which on recrystallisation from hot hexane, yielded white lustrous cubes, m p 167° C (0.1 gm), depressed to 150–52° C by admixture with the isomeride, m p 185° C. Finally, the benzene mother liquor gave a neutral brown sticky mass (2.6 gms), which could not be obtained in the solid form.

Condensation of p-nitrophenyl succinic anhydride with toluene and separation of β -p-nitrophenyl- β -p-toluoyl propionic and α -p-nitrophenyl- β -p-toluoyl propionic acids—The proportions used were, dry toluene (18 c.c.), the anhydride (6 gms) and anhydrous AlCl_3 (8 gms). The crude solid, on purification through 10% Na_2CO_3 , yielded a brownish solid, m p 120–30° C (4.8 gms). Treatment with hot benzene-petrol left a residue, m p 160–70° C, which on recrystallisation from methyl alcohol, gave small shining needles, m p 178° C (1.0 gm) depressed at 160° C by admixture with pure *p*-nitrophenyl succinic acid.

(Found C, 65.6, H, 4.9, N, 4.5. $\text{C}_{17}\text{H}_{15}\text{O}_5\text{N}$ requires C, 65.2, H, 4.7, N, 4.4%)

The benzene extract, on concentration, deposited first, the unchanged acid, m p 218° C (0.54 gm), then several fractions ranging from 155–70° (a), and finally a pale yellow gum (neutral), which could not be solidified (2.0 gms). The fractions (a) on repeated crystallisation from benzene, yielded small colourless cubes, m p 173° C (0.3 gms) depressed to 155–60° C. with the isomer 178° C and which formed both the pyrylium salt and the piperonal derivatives.

(Found C, 65.4, H, 4.8, N, 4.7 $C_{17}H_{16}O_5N$ requires C, 65.2, H, 4.7, N, 4.4%)

The benzene mother liquor, finally, gave on concentration, a mixture, m.p. 120–30° C (0.6 gm), from which, through piperonal condensation, 0.2 gm of the keto-acid m.p. 178° C was recovered.

Condensation of p-nitrophenyl succinic anhydride with toluene in nitrobenzene solution—The anhydride (10 gms) and dry toluene (30 c.c.) were condensed as usual, in presence of a solution of anhydrous aluminium chloride (12 gms) in nitrobenzene (50 c.c.) The crude product, on purification through sodium carbonate solution, yielded a brownish solid, m.p. 150–60° C (6 gms). On trituration with warm benzene-petrol, a white solid, m.p. 162–69° C was left, which on several crystallisations from hot benzene, deposited a fraction, m.p. 170–75° C. From methyl alcohol it yielded small shining needles, m.p. 178° C (1.0 gm), identified as β - β -substituted isomeride. The benzene mother liquor, on slow concentration, gave first, the unchanged acid, m.p. 218° C (0.1 gm), and then small lustrous cubes, m.p. 173° C (0.5 gm) identified as the α - β -form. On further concentration, it gave (3.0 gms) of a pale yellow gum (neutral), which could not be resolved into solid state.

(C) *Condensations with p-methoxyphenyl succinic anhydride*—*p*-Methoxyphenyl succinic acid was prepared from *p*-methoxybenzylidene cyanacetate and potassium cyanide according to the method of Lapworth and Macrae,⁶ and melted at 204° C. The anhydride prepared as usual, crystallised in small needles, m.p. 93° C.

Condensation of p-methoxyphenyl succinic anhydride with benzene—The anhydride (5 gms) and dry benzene (20 c.c.) were condensed as usual, in presence of anhydrous $AlCl_3$ (10 gms). A brown gummy mass (4.5 gms) was obtained, which after purification through 5% sodium bicarbonate was dissolved in hot benzene and on cooling yielded white needles, m.p. 158° C (1.07 gms).

(Found. C, 71.4, H, 5.8 $C_{17}H_{16}O_4$ requires C, 71.8, H, 5.6%)

The benzene mother liquor, on further concentration yielded a gum (3.3 gms), which was dissolved in alcohol and refluxed for 6 hours with an alcoholic solution of sodium acetate and semicarbazide hydrochloride. On dilution with water, a solid m.p. 170–220° C separated out, which on fractional crystallisation through benzene yielded (a) a semicarbazone, m.p. 248° C (1.2 gms.), identified as the derivative of α - β -isomer, by admixture with the pure specimen; (b) a neutral substance, m.p. above 290° C (0.3 gm.),

and (c) a gum (1.5 gms.) which could not be resolved into its components. The original acid mother liquor, on concentration, yielded *p*-methoxyphenyl succinic acid (0.5 g m)

Condensation of p-methoxyphenyl succinic anhydride with benzene in nitrobenzene solution—The anhydride (5 gms) and dry benzene (20 c c) were condensed as usual, in presence of anhydrous aluminium chloride (10 gms) in nitrobenzene (40 c c), and the excess of the solvent and benzene steam-distilled. The contents on cooling gave (a) a clear supernatant liquid, which on concentration, yielded the unchanged *p*-methoxy-phenyl succinic acid (0.5 gm) and (b) a gum which was taken up in ether, and extracted with 5% Na_2CO_3 . On acidification, a gum was obtained which was dried (4 gms) and treated with semicarbazide hydrochloride as usual. It yielded first (a) a neutral organic substance unmelted below 280°C (0.7 gm), and (b) yellowish long needles, m p 248°C (1.6 gms), identified as the semicarbazone of the α - β -isomeride, m p 158°C .

Piperonal as well as pyrylium salt reactions with the above keto-acid, gave in the first case, a pale yellow gum along with piperonyllic acid, and in the second case, a scarlet red powder, readily soluble in caustic soda solution, and not melting below 300°C .

Synthesis of α -p-methoxyphenyl- β -benzoyl propionic acid—Potassium cyanide (1.5 gms) dissolved in water (5 c c) was gradually added to a solution of *p*-methoxy chalcone (2 gms) in alcohol (40 c c). Glacial acetic acid (1 c c) was then added and the mixture kept at the room temperature overnight. When the solvent was distilled off, colourless leaflets of the nitrile, m p 121°C separated out. It was dissolved in 5 times its weight of concentrated sulphuric acid, and then water was added in drops till a faint but permanent turbidity was produced. The mixture was refluxed on the sand-bath, for four hours when a gum separated out. It was purified through 5% sodium carbonate, when a solid, m p 153°C was obtained which on recrystallisation, through alcohol, yielded colourless needles, m p 158°C . Its m p was not depressed by admixture with the pure α - β -isomeride.

Condensation of p-methoxyphenyl succinic anhydride with toluene—The proportions used were—the anhydride (5 gms.), toluene (20 c c.) and AlCl_3 (10 gms.). The crude acid, on purification through sodium bicarbonate, yielded a brownish semi-solid mass (5 gms), which when dried in vacuum, and crystallised from alcohol deposited a solid, m p. 120 – 30°C . On fractional crystallisation through benzene, white needles, m p. 147°C (1.6 gms) were obtained. With piperonal it gave a yellowish gum with piperonyllic

acid, and the original keto-acid was never recovered. In the pyrylium salt reaction, it gave a scarlet red solid, readily soluble in caustic soda, but unmelted below 300° C.

(Found: C, 72.8; H, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5%, H, 6.0%.)

The benzene mother liquors were dried and then mixed with the alcoholic mother liquor, which on further dilution, yielded first the acid, m.p. 147° C (0.6 gm.) and then a gum (a). The supernatant liquid, on concentration, yielded a solid, m.p. 153° C, which when recrystallised through benzene, gave a colourless crystalline solid, m.p. 158° C (0.6 gm.). It depressed the melting point of the keto-acid (α - β -form m.p. 147° C) to 130° C and failed to respond both to the piperonal and pyrylium salt reactions.

(Found: C, 72.3, H, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5, H, 6.0%.)

The gum (a) (1.7 gms.), which defied all our attempts to break up, was then treated with semicarbazide hydrochloride, and on dilution with water, yielded a solid (b) which when recrystallised from hot alcohol gave colourless cubes, m.p. 168° C (0.4 gm.) (c) a neutral organic substance, unmelted below 280° C (0.2 gm.) and then (d) a gum (1.0 gm.) which could not be crystallised out. The original mother liquor (acidic), on concentration, yielded the unchanged *p*-methoxy-phenyl succinic acid (0.5 gm.).

Condensation of p-methoxyphenyl succinic anhydride with toluene in nitrobenzene solution—5 gms. of the anhydride, 20 c.c. of dry toluene and 10 gms. of aluminium chloride anhydrous in 40 c.c. of nitrobenzene were used. The crude acid was taken up in ether, and extracted with 5% sodium carbonate solution. On acidification, a solid (4.0 gms.), was obtained which on fractional crystallisation through alcohol, gave white needles m.p. 147° C. (2.1 gms.) and a gum (1.9 gms.), which on treatment with semicarbazide hydrochloride and subsequent dilution with water, gave a neutral substance, not melting below 280° C (0.5 gm.) and then a gum (1.3 gms.), which could not be resolved into its components. The original mother liquor (acidic), on concentration, yielded the unchanged *p*-methoxy-phenyl succinic acid (0.6 gm.).

(D) *Condensations with p-chlorophenyl succinic anhydride*—

p-Chlorophenyl succinic acid was prepared from *p*-chlorobenzylidene cyanacetate and potassium cyanide according to the method of Lapworth and Macrae.⁶

p-Chlorobenzylidene cyanacetate was obtained by first preparing *p*-chlorotoluene, converting it into *p*-chlorobenzaldehyde and then condensing the latter, with cyanacetic ester in presence of piperidine. The nitrile, after

purification, was condensed with potassium cyanide and the product or subsequent hydrolysis, gave the crude acid, m p 195–97° C. On purification through 10% sodium carbonate, it gave a yellowish white solid, m p. 200–01° C. which on recrystallisation from ethylacetate, yielded colourless cubes of *p*-chlorophenyl succinic acid, m p 205° C, insoluble in benzene and cold water, and soluble in hot water and ethylacetate

(Found C, 52.3, H, 3.6; Cl, 15.5 C₁₀H₇O₄Cl requires C, 52.5, H, 3.9, Cl 15.5%)

p-Chlorophenyl succinic anhydride prepared as usual, from phenyl succinic acid and acetic anhydride crystallised from hot petroleum ether into long colourless needles, m p 80° C

Condensation of p-chlorophenyl succinic anhydride with benzene and separation of β-p-chlorophenyl-β-benzoyl propionic and α-p-chlorophenyl-β-benzoyl propionic acids—The proportions used were, the anhydride (6 gms), dry benzene (18 c c) and anhydrous aluminium chloride (8 gms) The crude brownish mass, on purification through sodium carbonate, yielded a solid (4 gms), m p 80–100° C, which on treatment with benzene, gave an insoluble residue, m p 120–30° C (a) On crystallisation from hot benzene and then dilute methyl alcohol, the fraction, (a) yielded lustrous plates, m p 166° C (0.6 gm), depressed to 150° C by admixture with the original acid

(Found C, 66.1, H, 4.5, Cl, 12.1 C₁₈H₁₃O₃Cl requires C, 66.5, H, 4.5, Cl, 12.3%)

The benzene mother liquor was mixed with that from the fraction (a), and on concentration, first deposited a fraction, m p 158–62° C (b), and then another fraction, m p 138–40° C (c) The fraction (b) yielded the keto-acid, m p. 166° C. (0.1 gm), and a fraction (c) gave on similar treatment small shining needles, m p 146° C (0.6 gm) depressed to 127° C. by mixing with the isomer, m p 166° C and to 130° C with the original acid. It also gave the characteristic pyrylium and piperonylidene salt reactions.

(Found C, 66.1, H, 4.5; Cl, 12.0. C₁₈H₁₃O₃Cl requires C, 66.5; H, 4.5, Cl, 12.3%)

The final mother liquor, on concentration, gave a pale yellow gum (2.5 gms), a neutral substance, which could not be obtained in the solid form

Condensation of p-chlorophenyl succinic anhydride with benzene in nitrobenzene solution.—The proportions used were, the anhydride (6 gms.), dry

benzene (18 c c) and anhydrous aluminium chloride (10 gms) in nitrobenzene (50 c c) The contents of the flask after steam distillation, deposited a black sticky mass (a), and shining needles, m p 205°C (1.5 gms) identified as the unchanged acid. The crude product (a), on purification through 10% sodium carbonate solution, yielded a sticky mass, m p $80\text{--}100^{\circ}\text{C}$, which when triturated with hexane, deposited a brownish solid, m p $120\text{--}60^{\circ}\text{C}$ On several crystallisations from (dilute) ethyl alcohol, it yielded a very small amount of the keto-acid, m.p 166°C (0.1 gm) and the unchanged *p*-chlorophenyl succinic acid (1.2 gms) The final alcoholic mother liquor gave a brownish sticky mass, from which nothing definite could be obtained

Reduction of β -phenyl- β -p-toluoyl propionic acid by Clemmensen method, and isolation of Y-p-tolyl- β -phenyl butyric acid—A mixture of the keto-acid (1 gm), zinc amalgam (10 gms) and (con) HCl was used in the reaction The crude sticky mass, on purification through 10% sodium carbonate, gave a white solid, m p $70\text{--}75^{\circ}\text{C}$ Repeated crystallisation from petroleum ether gave ultimately, small needles, m p 104°C . (0.8 gm)

(Found: C, 79.8, H, 7.1 $\text{C}_{17}\text{H}_{18}\text{O}_2$ requires C, 80.3, H, 7.1%)

Reduction of β -p-chlorophenyl- β -benzoyl propionic acid, was effected by Clemmensen method The crude solid on purification through sodium carbonate yielded a solid, m p $83\text{--}85^{\circ}\text{C}$, which when recrystallised from petroleum ether, gave short colourless needles, m p 86°C of Y-phenyl- β -p-chlorophenyl butyric acid

(Found: C, 69.4; H, 5.4, Cl, 12.6 $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Cl}$ requires C, 69.8, H, 5.4, Cl, 12.9%)

Reduction of α -p-chlorophenyl- β -benzoyl propionic acid, was effected in similar way. The white solid, m p. $140\text{--}45^{\circ}\text{C}$. was obtained which on recrystallisation from benzene gave lustrous needles of Y-phenyl- α -p-chlorophenyl butyric acid, m.p. 150°C depressed to 120°C by the original keto-acid.

(Found: C, 69.3, H, 5.4; Cl, 12.6. $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Cl}$ requires, C, 69.8; H, 5.4; Cl, 12.9%)

Summary

The influence of the *p*-nitrophenyl, *p*-methoxyphenyl, and *p*-chlorophenyl groups (in *p*-substituted phenyl succinic acid) compared to that of the phenyl group (in phenyl succinic acid) has been studied in condensations with simple aromatic hydrocarbons and the results have been embodied in Tables I and II

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THE REDUCTION OF $-\text{CH}(\text{OH})\text{CCl}_3$ GROUP ATTACHED TO A BENZO- α -PYRONE NUCLEUS

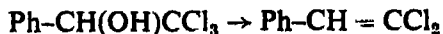
BY D R KULKARNI AND N M SHAH

(From the Department of Chemistry, Karnatak College, Dharwar, and
M R Science Institute, Gujarat College, Ahmedabad)

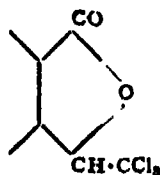
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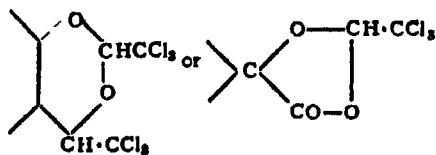
THE reduction of $-\text{CH}(\text{OH})\text{CCl}_3$ group in trichloro-methyl carbinols present as such or potentially formed during the course of reduction from trichloro-methylphthalide ring (A) or the heterocyclic ring (B) has been an interesting subject for investigation by numerous workers. Using zinc and boiling alcohol, Jocitsch¹ found that the reaction took the course thus



The best results were obtained by reducing the acetyl derivative, using the zinc in form of its shavings. Jocitsch also studied the tertiary alcohols containing the group $\text{>C}(\text{OH})\text{CCl}_3$. According to his method of reduction, the group $-\text{CH}(\text{OH})\text{CCl}_3$ is converted into $-\text{CH}=\text{CCl}_2$, and the group $\text{>C}(\text{OH})\text{CCl}_3$ into $\text{>C}=\text{CCl}_2$.



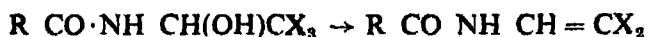
(A)



(B)

Using zinc dust and glacial acetic acid as reducing agents, Meldrum and Alimchandani² observed that in several compounds investigated by them, the group $-\text{CH}(\text{OH})\text{CCl}_3$ is reduced with the production of $-\text{CH}_2\text{CHCl}_2$ group. In extending their study of this reduction, Meldrum and his several collaborators³ applied it to a large number of compounds including those of the type (A) and (B) shown above. On the other hand, Wheeler and

Yelburgi⁴ proved that the group $-\text{CH}(\text{OH})\text{CX}_2$ ($\text{X} = \text{Cl}$ or Br) is reduced to $-\text{CH}=\text{CX}_2$ and not to $-\text{CH}_2\text{CHX}_2$ in case of chloral- and bromal-amides

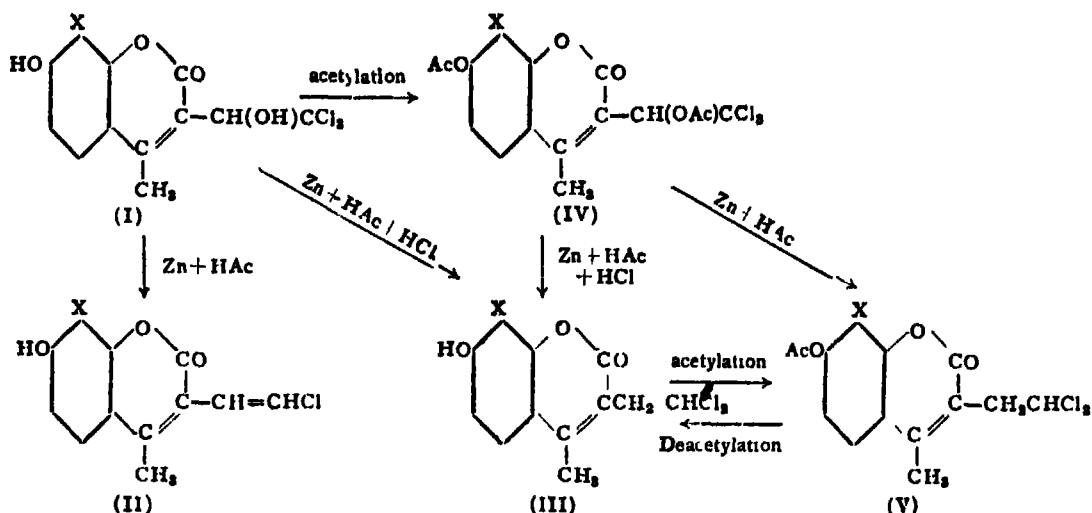


Recently Dharwarkar and Alimchandani⁵ have shown that in the case of some chloral-hydroxy-benzoic acid derivatives, the group $-\text{CH}(\text{OH})\text{CCl}_2$ gets reduced to the unsaturated group $-\text{CH}=\text{CCl}_2$, and not to the saturated group $-\text{CH}_2\text{CHCl}_2$ as erroneously postulated by Meldrum and collaborators. It is clear from the brief survey given above that in all the cases investigated hitherto, the group $-\text{CH}(\text{OH})\text{CCl}_2$ is present either in the open-chain derivatives or is attached to an aromatic nucleus

During the course of our studies on the effect of α -substituents in the Pechmann condensation, a number of benzo- α -pyrones (coumarins) containing $-\text{CH}(\text{OH})\text{CCl}_2$ group in 3-position of the pyrone ring were synthesised by Kulkarni, Alimchandani and Shah⁶. Because the reduction of $-\text{CH}(\text{OH})\text{CCl}_2$ group attached to a benzo- α -pyrone nucleus is hardly known, a study of the reduction of various 3- $-\text{CH}(\text{OH})\text{CCl}_2$ -substituted coumarin derivatives synthesised by Kulkarni, Alimchandani and Shah was undertaken by the present authors, the reducing agents used being zinc dust and glacial acetic acid, (a) in conjunction with concentrated hydrochloric acid and (b) without the hydrochloric acid

7-Hydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin (I) on reduction by zinc dust and acetic acid gave 7-hydroxy-3-(β -chloro-vinyl)-4-methyl-coumarin (II). On carrying out the same reduction in conjunction with conc. hydrochloric acid, 7-hydroxy-3-($\beta\beta$ -dichloro-ethyl)-4-methyl-coumarin (III) was obtained. Evidently, the addition of hydrochloric acid to the β -chloro-vinyl group produced by the reduction takes place with the ultimate production of the $-\text{CH}_2\cdot\text{CHCl}_2$.

The acetyl derivative of (I), 7-acetoxy-3-(α -acetoxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin (IV) on similar reduction by zinc and acetic acid gave 7-acetoxy-3-($\beta\beta$ -dichloro-ethyl)-4-methyl-coumarin (V) identical with the acetoxy derivative of (III), which is obtained directly by the reduction of (IV) in presence of conc. hydrochloric acid. The results are shown diagrammatically below. ($\text{X} = \text{H}$ in all compounds in this series)



7 8-Dihydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methyl-coumarin (I ; X = OH) behaves exactly similarly, it gave 7 8-dihydroxy-3-(β -chloro-vinyl)-4-methylcoumarin (II, X = OH) and 7 8-dihydroxy-3-($\beta\beta$ -dichloroethyl)-4-methylcoumarin (III, X = OH) when reduced without and with conc hydrochloric acid respectively. The acetoxy derivative (IV, X = OAc) on reduction by zinc and acetic acid only gave V (X = OAc) identical with the acetyl derivative of the coumarin III (X = OH), obtained directly on reduction in presence of conc hydrochloric acid of the acetoxy derivative (IV).

The reduction of 5-hydroxy-4 7-dimethyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-coumarin also takes a similar course on reduction by zinc and acetic acid (a) without conc hydrochloric acid and (b) in the presence of the acid, it gave (a) 5-hydroxy-4 7-dimethyl-3-(β -chloro-vinyl)- and (b) 3-($\beta\beta$ -dichloroethyl)-coumarin derivatives respectively.

5 7-Dihydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin on reduction by zinc and acetic acid gave a product which could not be crystallised. But its acetoxy derivative was smoothly reduced by zinc and acetic acid to 5 7-diacetoxy-3-($\beta\beta$ -dichloro-ethyl)-4-methyl coumarin, which was deacetylated to the corresponding 5 7-dihydroxy-derivative.

4-Methyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-1,2- α -naphtha-pyrone and 4,6-dimethyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-coumarin gave only one type of the reduction product, viz, 3-($\beta\beta$ -dichloroethyl), whether hydrochloric acid was used or not during the reduction as in the previous cases.

From the above results and those of the previous investigators on the reduction of $-\text{CH}(\text{OH})\text{CCl}_3$ group, it is evident that the reduction does not

proceed in a uniform manner in all cases. It is highly affected by the constitutional factors. A study of the reduction products of $-\text{CH}(\text{OH})\text{CCl}_3$ present in several coumarins described in this paper supports the above point. The following generalisation of the results described in this communication reveals some interesting points:

(a) On reduction with zinc and acetic acid, the group $-\text{CH}(\text{OH})\text{CCl}_3$ in the pyrone ring is reduced to $-\text{CH}=\text{CHCl}$ group in case of hydroxycoumarins, i.e., those obtained from resorcinol, pyrogallol, etc.

(b) The same group $-\text{CH}(\text{OH})\text{CCl}_3$ is reduced to $-\text{CH}_2\text{CHCl}_2$ when

(i) the reduction is carried out in conjunction with concentrated hydrochloric acid, &

(ii) the phenolic group ($-\text{OH}$) is absent, as in case of coumarins obtained from α -naphthol and *p*-cresol; and

(iii) the phenolic $-\text{OH}$ group is protected by acetylation

Experimental

(A) Reduction of 7-hydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin

1 *Formation of 7-hydroxy-3-(β -chloro-vinyl)-4-methylcoumarin*—This reduction was carried out by means of zinc dust and acetic acid according to the details of Kulkarni, Alimchandani and Shah⁶. The reduction product obtained melted at $254\text{--}55^\circ$ (decomp.) not depressed by mixture with the sample of those authors.

2 *Formation of 7-hydroxy-3-($\beta\beta$ -dichloro-ethyl)-4-methylcoumarin*—(a) The coumarin (2 g) was dissolved in hot glacial acetic acid (30 c.c.) and the solution mixed with conc. HCl (6–7 c.c.). Zinc dust (2 g) was gradually added with stirring. After reaction subsided, the solution was boiled for a few minutes, filtered from the unchanged zinc and the filtrate diluted with water. The reduction product was collected and crystallised from dil. alcohol, yellowish needles, m.p. $206\text{--}07^\circ$. [Found: Cl, 26.29; $\text{C}_{12}\text{H}_{10}\text{O}_3\text{Cl}_2$ requires Cl, 26.02 per cent.]

(b) 7-Acetoxy-3-(α -acetoxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin was similarly reduced as above. The reduction product was found to be identical with the above product.

3 *Formation of 7-acetoxy-3-($\beta\beta$ -dichloro-ethyl)-4-methylcoumarin*—(a) The above reduction product (0.5 g) was dissolved in acetic anhydride (7 c.c.) in presence of conc. sulphuric acid (4 drops). The clear solution was shaken for about 10–15 minutes and poured into water. The solid was collected and

crystallised from rect spirit, rhombic plates, m p $101-102^\circ$ [Found Cl, 22.9; $C_{14}H_{12}O_4Cl_2$ requires Cl, 22.54 per cent] It does not exhibit any fluorescence

(b) The above substance was also obtained directly by reducing 7-acetoxy-3-(α -acetoxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin (0.5 g) by adding zinc dust (0.7 g) to its acetic acid solution in the usual way, m p. $101-102^\circ$ (yield 0.3 g). The mixed melting point of this compound with the derivative obtained by (a) was unchanged

4 *De-acetylation of the above acetoxy derivative*—The acetoxy derivative (1 g) was suspended in methyl alcohol (10 c c) and conc H_2SO_4 (8 c c) added, the mixture was refluxed on water-bath for an hour and a half. After cooling, it was diluted with water and the substance obtained crystallised from acetic acid (animal charcoal), m p $206-207^\circ$, the mixed m p with 7-hydroxy-3-($\beta\beta$ -dichloro-ethyl)-4-methylcoumarin obtained above remaining undepressed

(B) *Reduction of 7 : 8-dihydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-4-methylcoumarin*

1 *Formation of 7 : 8-dihydroxy-3-(β -chloro-vinyl)-4-methylcoumarin*—The procedure followed by Kulkarni, Almchandan and Shah⁶ was employed and the reduction carried out as usual. The reduction product crystallised from alcohol, needles, m p. $231-232^\circ$. The mixed melting point was also undepressed

2 *Formation of 7 : 8-dihydroxy-3-($\beta\beta$ -dichloro-ethyl)-4-methylcoumarin*—(a) The coumarin (8 g) dissolved in acetic acid (100 c c) and mixed with conc HCl (30 c c) was slowly treated with zinc (7 g). Vigorous reaction took place. When the reaction subsided, the unchanged zinc was removed and the filtrate diluted with water. The product crystallised from acetic acid and then from benzene, hexagonal prisms, m p $195-196^\circ$, yield 5 g. [Found Cl, 24.73, $C_{12}H_{10}O_4Cl_2$ requires 24.52 per cent]

(b) The same reduction product was obtained by carrying out the reduction of 7 : 8-di-acetoxy-3-(α -acetoxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin in presence of conc HCl as before.

The acetyl derivative prepared by acetic anhydride-pyridine method crystallised from alcohol, needles, m.p. $163-164^\circ$. [Found: Cl, 18.88, $C_{14}H_{14}O_6Cl_2$ requires Cl, 19.0 per cent]

The same acetyl derivative was obtained by the reduction of 7 : 8-di-acetoxy-3-(α -acetoxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin using zinc dust and acetic acid as usual.

The de-acetylation of the substance by conc sulphuric acid in methyl alcoholic solution gave the corresponding 7-8-di-hydroxy-coumarin identical in all respects with the same substance described already

(C) *Reduction of 5-hydroxy-4-7-dimethyl-3-(α -hydroxy- $\beta\beta$ -trichloro-ethyl)-coumarin.*

1 *Formation of 5-hydroxy-4-7-dimethyl-3-(β -chloro-vinyl)-coumarin*—

The coumarin (1 g) was suspended in hot acetic acid (15 c c) and zinc dust (1 g) added gradually as in previous cases. As the reaction proceeded, the substance went into solution. The reduction product was isolated as before and crystallised from dil alcohol, diamond-shaped crystals, m p 251–52° [Found Cl, 14.24; $C_{13}H_{11}O_3Cl$ requires Cl, 14.16 per cent]

The *acetyl* derivative obtained by acetic anhydride-pyridine method (2½ hours refluxing on water-bath) crystallised from alcohol in needles, m.p. 148–49°. [Found Cl, 11.92, $C_{15}H_{13}O_4Cl$ requires Cl, 12.12 per cent]

2 *Formation of 5-hydroxy-4-7-dimethyl-3-($\beta\beta$ -di-chloro-ethyl)-coumarin*

—The above reduction was carried out in presence of conc HCl (4 c c) and the reduction product isolated as before, first crystallised from alcohol and then from ethyl acetate, needles, m.p. 242° [Found Cl, 24.83, $C_{13}H_{12}O_3Cl_2$ requires Cl, 24.69 per cent]

The *acetyl* derivative prepared as before crystallised from dilute alcohol, rectangular plates, m p 157° [Found Cl, 21.30, $C_{15}H_{14}O_4Cl_2$ requires Cl, 21.54 per cent]

(D) *Formation of 5-7-di-acetoxy-3-($\beta\beta$ -dichloro-ethyl)-4-methylcoumarin*

5-7-Diacetoxy-3-(α -acetoxy- $\beta\beta\beta$ -trichloro-ethyl)-4-methylcoumarin (2 g) was reduced by means of zinc dust (2.5 g) and acetic acid (25 c c) as in previous cases. The product crystallised from dil. alcohol, rectangular rods, m p 121–22°. [Found Cl, 18.91, $C_{16}H_{14}O_6Cl_2$ requires Cl, 19.0 per cent]

De-acetylation of the above 5-7-diacetoxy-coumarin derivative—The de-acetylation was effected by sulphuric acid (7 c c) in methyl alcohol solution (1 g in 10 c c) by refluxing for 1½ hours on water-bath. The solution was diluted with water and the substance obtained crystallised from dil. alcohol, thin flakes, m p 246–47° [Found Cl, 24.67, $C_{12}H_{10}O_4Cl_2$ requires Cl, 24.52 per cent]

(E) *Formation of 4-methyl-3-($\beta\beta$ -di-chloroethyl)-1-2- α -naphtha-pyrone*

4-Methyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloro-ethyl)-1-2- α -naphtha-pyrone (2.5 g) was reduced by zinc (2.5 g) in its acetic acid solution (30 c c) and the product isolated as before. It first crystallised from dichlorobenzene and

then from xylene, m p 221–22° (yield, 1.5 g) [Found Cl, 22.71, $C_{16}H_{13}O_2Cl_3$ requires Cl, 23.09 per cent]

The same product was obtained by carrying out the reduction in presence of conc. HCl (4 c.c. for 1 g. of the coumarin)

Formation of 4:6-dimethyl-3-($\beta\beta$ -dichloro-ethyl)-coumarin—4:6-Dimethyl-3-(α -hydroxy- $\beta\beta$ -trichloro-ethyl)-coumarin (1 g.) was reduced as before (zinc 1 g. + acetic acid 15 c.c.) The product crystallised from alcohol in rectangular plates, m p 206–07° [Found Cl, 25.84, $C_{13}H_{12}O_2Cl_3$ requires Cl, 26.16 per cent]

A better yield is obtained if the above reduction is carried out in conjunction with conc. HCl (4 c.c. for 1 g. of the coumarin)

We thank Prof. M. S. Shah and Prof. R. L. Alimchandani for their interest and facilities for the work. We are grateful to Dr. R. C. Shah for his useful suggestions and interest in the investigation.

Summary

The reduction of $-CH(OH)CCl_3$ group attached to a benzo- α -pyrone nucleus has been studied for the first time, the reducing agents used being zinc dust and glacial acetic acid either in conjunction with conc. HCl or without it. It is found that the course of the reduction is highly affected by the constitutional factors. The following generalisation is made in this connection:

(a) on reduction with zinc and acetic acid, the group $-CH(OH)CCl_3$ in the pyrone ring is reduced to $-CH=CHCl$ group in case of hydroxy-coumarins, (b) the same group $-CH(OH)CCl_3$ is reduced to $-CH_2CHCl_2$ group if (i) the reduction is carried out in conjunction with conc. HCl, (ii) the phenolic group $-OH$ is either absent or is protected by acetylation.

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PYRONINE DYESTUFFS DERIVED FROM SUCCINIC ACID

BY SIKHIBHUSHAN DUTT

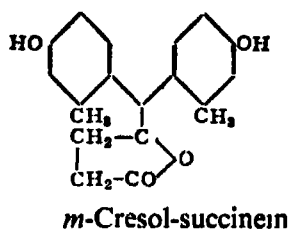
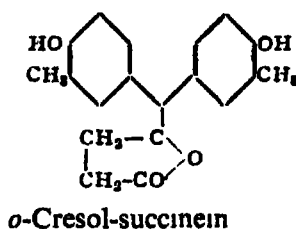
(From the Chemical Laboratory, Allahabad University)

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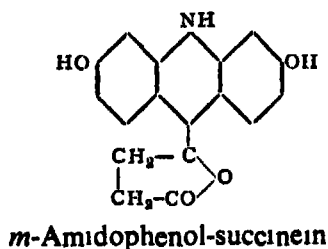
RESORCINOLSUCCINEIN or what is commonly known as succinyl-fluorescein has been known in an impure condition ever since Baeyer¹ prepared ordinary fluorescein or resorcinol-phthalein by the action of phthalic anhydride on resorcinol. In 1923 Biggs and Pope² obtained resorcinol-succinein in a pure condition and in the following year Dutt and Thorpe³ were successful in getting it in a finely crystalline form. The same authors also prepared succinyl-rhodamine or *m*-dimethylamidophenol-succinein hydrochloride in glistening needles, having properties almost identical with ordinary rhodamine or *m*-dimethylamidophenol-phthalein hydrochloride. Two years later on, that is in 1926, Dutt⁴ prepared phenol-succinein for the first time as colourless prisms melting at 252° C, and dissolving in dilute sodium hydroxide with intense crimson colour, just like ordinary phenol-phthalein. A large number of analogous derivatives of succinic acid were prepared by the same author by condensation of the anhydride with aromatic phenols and amino compounds, and the results although incorporated in the thesis for the degree of Doctorate of Science of the London University, were not subsequently published in consideration of the fact, that, as the most important compounds of the series had already been published, the analogous compounds were not of sufficient importance to deserve publication by themselves. But in view of a recent paper by Dass and Tewari⁵ describing many of these analogous succineins and containing results which are not only highly surprising but are beyond all normal expectations, that the present author has thought it necessary and desirable to publish his own experimental results carried out in this connection in the London University nearly 16 years ago and also corroborated by recent experiments carried out in India. The results have been tabulated at the end of the experimental portion of the paper, and for the sake of comparison have been grouped against the corresponding results of Dass and Tewari and also against known data regarding the corresponding phthaleins.

The most remarkable feature about the work of Dass and Tewari mentioned above with regard to the succineins is that they have described the

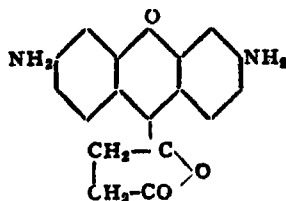
greater majority of them as a series of *black powders*, whereas the present author could only isolate them as colourless crystalline substances, just like the corresponding phthaleins *O*-cresol-succinein and *m*-cresol-succinein have been given the molecular formula of $C_{16}H_{16}O_3$ by Dass and Tewari which is definitely wrong, since undoubtedly they possess the following molecular structures :



and therefore the molecular formula $C_{16}H_{16}O_4$. Similar is the case with the compound, *m*-amidophenol-succinein, which they have described as a violet powder soluble in caustic soda and insoluble in acids. The formula that Dass and Tewari have given to the substance, that is $C_{16}H_{14}O_3N_2$, is apparently wrong, as it is undoubtedly phenolic in character and therefore possesses the molecular structure given below —



which corresponds to the formula $C_{16}H_{13}O_4N$. Had the authors determined the nitrogen content of their compound, they would have easily found out their mistake. The structural formula assumed by Dass and Tewari for their substance, that is :



is incompatible with the properties of the compound described by themselves since with the above formula, it is not possible even by a stretch of imagination

to visualise how the substance could dissolve in caustic soda and get precipitated by acids. On the contrary one would easily think that with such a formula which is that of a true rhodamine, this substance would, like a rhodamine, get easily dissolved in acids and precipitated by alkalies. Apparently the authors are not aware of the fact that *m*-amidophenol condenses with dibasic acid anhydrides in a different way to that of *m*-dimethyl amidophenol, and the two condensation products have different properties. This has already been clearly shown by Dutt⁶ as early as 1923.

Experimental

O-Cresol-succinein—This was prepared by heating *o*-cresol with succinic anhydride in presence of stannic chloride in the same way as phenol-succinein (Dutt⁴). Two products were simultaneously formed, one being *o*-cresol-succinein (major fraction) and the other *o*-cresol-succinein-anhydride, and they were separated from each other by the action of caustic soda in which the former only is soluble.

O-Cresol succinein crystallises from alcohol in colourless prisms melting at 264° C and dissolving in alkalies with an intense crimson colour (Found C = 72.3, H = 6.3. $C_{18}H_{18}O_4$ requires C = 72.5, H = 6.0%).

O-Cresol-succinein-anhydride crystallises from glacial acetic acid in colourless glistening needles melting at 178–79° C and is insoluble in alkalies or ammonia. It has properties very similar to *o*-phenol-phthalein-anhydride or fluoran first prepared by Baeyer⁷ in 1892 (Found C = 76.8, H = 5.9. $C_{18}H_{16}O_3$ requires C = 77.1, H = 5.7%).

M-Cresol-succinein—This was prepared from succinic anhydride and *m*-cresol in the same way as *o*-cresol-succinein. It crystallises from dilute alcohol in colourless glistening prisms melting at 146° C and dissolves in dilute alkalies and ammonia with a bright pink colour. (Found C = 72.2; H = 6.2. $C_{18}H_{18}O_4$ requires C = 72.5, H = 6.0%.)

• ***α*-Naphthol-succinein**—This was prepared by heating a mixture of succinic anhydride (10 g), *α*-naphthol (14 g) and chlorosulphonic acid (5 g) at 100–110° C for 4 hours in a stream of carbon dioxide. The melt was then poured into a litre of boiling water and the insoluble grey precipitate filtered off and repeatedly crystallised from alcohol with the addition of animal charcoal ultimately as colourless needles melting at 245° C. It dissolves in dilute alkalies and ammonia with an intense blue colour. (Found C = 81.6, H = 4.8. $C_{24}H_{18}O_4$ requires C = 81.8, H = 4.5%.)

Quinol-succinein.—This was prepared by heating a mixture of succinic anhydride (10 g), quinol (22 g) and concentrated sulphuric acid (1 c.c.) at

160–170° C for 6 hours in a current of carbon dioxide. The melt was poured into boiling water and the insoluble precipitate crystallised from dilute alcohol with the addition of animal charcoal in colourless glistening prisms melting at 258° C. It dissolves in dilute alkalis and ammonia with an intense violet colour, which however soon oxidises and becomes ultimately brownish-yellow. (Found C = 67.3, H = 4.5. $C_{16}H_{12}O_8$ requires C = 67.6, H = 4.2%.)

Catechol-succinein—This was prepared from catechol and succinic anhydride in the same way as catechol-citraconein (Dhar and Dutt⁹), catechol itaconein (Dhar and Dutt⁹) or catechol- β -phenylpyridine-dicarboxylein (Tewari and Dutt¹⁰). The substance crystallises from alcohol in colourless glistening prisms melting at 286° C. It dissolves in caustic alkalis and ammonia with a transient green colour, which rapidly becomes brown by oxidation, particularly on exposure to the air. In all these respects, catechol-succinein is perfectly analogous to catechol-phthalein first prepared by Meyer¹¹ in 1905. (Found C = 67.2, H = 4.4. $C_{16}H_{12}O_8$ requires C = 67.6, H = 4.2%.)

Pyrogallol succinein—This was prepared from pyrogallol and succinic anhydride in the same way as quinol-succinein. It crystallises from dilute alcohol in colourless glistening prisms melting at 276° C. It dissolves in dilute alkalis and ammonia with a blue colour. (Found C = 60.4, H = 4.1. $C_{16}H_{12}O_7$ requires C = 60.7, H = 3.8%.)

Phloroglucinol-succinein—This was prepared from succinic anhydride and phloroglucinol in the same way as resorcinol succinein. It crystallises from dilute alcohol acidified with hydrochloric acid in bright orange-yellow prisms melting above 300° C. (Found C = 60.5, H = 4.1. $C_{16}H_{12}O_7$ requires C = 60.7, H = 3.8%.)

m-Amidophenol-succinein—This was prepared from *m*-amidophenol and succinic anhydride in the same way as 2,2'-iminophenol-sulphamphthalein (Dutt¹²). The substance crystallises from dilute alcohol in light-brown prisms melting at 224° C. It dissolves in dilute alkalis and ammonia with a brownish yellow-colour, but without any fluorescence. The alcoholic and acetic acid solutions are brownish-yellow with moss-green fluorescence. (Found N = 4.8, $C_{16}H_{13}O_4N$ requires N = 4.98%.)

m-Phenylenediamine-succinein—This was prepared from *m*-phenylenediamine hydrochloride and succinic anhydride in the same way as the corresponding camphorein (Sircar and Dutt¹³). The substance crystallised from dilute alcohol in bright yellow glistening plates melting at 242° C. It is insoluble in alkalis or ammonia, but dissolves in dilute acids with an intense orangecoloured colour. (Found: N = 15.3, $C_{16}H_{14}O_2N_2$ requires N = 14.9%.)

TABLE I

General Properties of the Succineins

(D = prepared by Dutt DT = prepared by Dass and Tewari
S = succinein)

Name of the compound	Appearance	M P. (° C)	Colour in alcohol	Colour in alkali
Phenol—S (D)	Colourless prisms	252	Colourless	Crimson
Do (DT)				
O-cresol—S (D)	Colourless prisms	264	Colourless	Crimson
Do (DT)	Chocolate-brown powder	195 blacken, 230 melt	Chocolate-brown	Reddish-violet
M-cresol—S (D)	Colourless prisms	146	Colourless	Crimson
Do (DT)	Light brown powder	112	Brownish-orange	Brownish-orange
α -Naphthol—S (D)	Colourless prisms	245	Colourless	Deep blue
Do (DT)	Black powder	185	Pink-orange	Pink-orange
Resorcinol—S (D)	Brown needles	234	Yellow	Orange-yellow
Do (DT)
Catechol—S (D)	Colourless prisms	286	Colourless	Transcient green
Do. (DT)	Black powder	Above 290	Dirty greenish-yellow	Dull green
Quinol—S (D)	Colourless prisms	258	Colourless	Transcient violet
Do (DT)
Pyrogallol—S (D)	Colourless prisms	276	Colourless	Blue
Do. (DT)	Grey-black powder	Above 290	Deep mahogany-brown	Violet
Phloroglucinol—S (D)	Orange-yellow prisms	Above 290	Orange-yellow	Orange-red
Do (DT)
M-amidophenol—S (D)	Light brown prism	224	Brownish-yellow	Brownish-yellow
Do (DT)	Violet powder	198	Violet-red	Violet-red
M-dimethylamido-phenol—S (HCl) (D)	Brown needles	225–30	Bluish-red	Insoluble
Do (DT)
M-phenylenediamine—S (D)	Yellow plates	242	Yellow	Insoluble
Do (DT)	Clay-coloured powder	210	.	..

TABLE II

Colour and Absorption Maxima of the Succineins

(D = prepared by Dutt DT = prepared by Dass and Tewari.

S = Succinein P = Phthalein)

Name of the compound	Colour in alcohol	Absorption maxima in ditto (Å)	Colour in alkali	Absorption maxima in ditto (Å)
Phenol—S (D)	Colourless		Crimson	5450
Do —S (DT)				5450
Do —P	Colourless		Crimson	5550
O-cresol—S (D)	do		do	5460
Do. —S (DT)	Chocolate-brown	4800	Reddish-violet	6250
Do —P	Colourless		Crimson	5565
M-cresol—S (D)	do		do.	5450
Do. —S (DT)	Brownish-orange	4000	Brownish-orange	4000
Do —P	Colourless		Crimson	5555
α-naphthol—S (D)	do		Deep blue	6080
Do —S (DT)	Pink-orange	4400	Pink-orange	4850
Do —P	Colourless		Deep-blue	6100
Resorcinol—S (D)	Yellow	4709	Orange	4936
Do. —S (DT)		5000		5200
Do —P	Yellow	4800	Orange	4940
Catechol—S (D)	Colourless		Green	6500
Do. —S (DT)	Dirty greenish-yellow	4300	Dull green	4600
Do. —P	Colourless		Green	6650
Quinol—S (D)	do		Violet	5810
Do —S (DT)				
Do. —P	Colourless		Violet	5900
Pyrogallol—S (D)	do		Blue	5950
Do. —S (DT)	Deep mahogany	5970	Violet	6750
Do. —P	Colourless		Blue	5980

TABLE II—*Contd*

Name of the compound	Colour in alcohol	Absorption maxima in ditto (Å)	Colour in alkali	Absorption maxima in ditto (Å)
Phloroglucinol—S (D)	Orange-yellow	4800	Orange	4920
Do —S (DT)				
Do —P	Orange-yellow	4850	Orange	4980
M-amidophenol—S (D)	Brownish-yellow	4750	Brownish-yellow (acid)	4800 (acid)
Do —S (DT)	Violet-red	5900	Violet-red (, ,)	5950 (, ,)
Do —P	Brown	4850	Brown (, ,)	4910 (, ,)
M-dimethylamido-phenol—S (HCl) (D)	Bluish-red	5465	Bluish-red (, ,)	5465 (, ,)
Do —S (DT)				
Do —P (HCl)	Deep pink	5550	Deep pink (, ,)	5550 (, ,)
M-phenylene-diamine—S (D)	Yellow	4550	Orange-red (, ,)	5000 (, ,)
Do —S (DT)		4450		4750 (, ,)

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ON THE CYANOGEN HALIDES

BY P KAILASAM

(From the Chemistry Department, Madras Christian College)

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I Action of Halogens on Cyanogen Halides

No observations appear to have been recorded on the action of halogens on cyanogen halides except that of chlorine on cyanogen chloride (Wurtz, 1851, Naumann and Vogt, 1870) and bromine on cyanogen bromide in ether (Poonamarew, 1885) which polymerise them to cyanuric chloride and cyanuric bromide respectively. The object of the present investigation is to study the possible displacement reactions with the cyanogen halides.

The action of chlorine gas on cyanogen iodide and the action of bromine on cyanogen chloride were first studied. It was expected that chlorine would displace iodine from cyanogen iodide forming cyanogen chloride, but it was found that cyanogen iodide was not affected by dry chlorine. Dry cyanogen iodide, prepared by warming an intimate mixture of one part of iodine and two parts of AgCN, at about 40°, was sublimed into a narrow tube which could be heated in a water-bath. Dry chlorine was passed through the tube for nearly two hours. No immediate reaction occurred, and even after leaving for a week at room temperature (30°) the white needles of cyanogen iodide remained unchanged. The tube was then slowly heated, but no reaction occurred up to the sublimation temperature of cyanogen iodide (about 40°). It was found that cyanogen iodide could be sublimed unchanged in an atmosphere of dry chlorine.

Since chlorine does not displace iodine from cyanogen iodide, it was thought that bromine might displace chlorine from cyanogen chloride forming cyanogen bromide. This reaction, however, is not simple.

Experimental

Cyanogen chloride was produced by the action of chlorine on aqueous hydrocyanic acid (10-15%) prepared by distilling potassium ferrocyanide with dilute sulphuric acid. The aqueous HCN was placed in a series of gas washing bottles containing glass beads. The last wash bottle was connected to a U-tube of calcium chloride which was sealed to a glass spiral cooled in

ice and salt. A steady current of chlorine was then passed through the aqueous hydrocyanic acid. The cyanogen chloride formed condensed in the spiral as a colourless liquid. The liquid CNCl was then purified by passing excess of chlorine to remove any free HCN , treated with pure dry mercury to remove the excess of chlorine, and finally distilled through sodium bicarbonate and calcium chloride to remove HCl and moisture respectively (Price and Green, 1920).

The reaction between bromine and cyanogen chloride was allowed to take place in a U-tube with taps sealed at either end. The bromine was distilled over fused calcium bromide into the apparatus and then the cyanogen chloride was distilled into the same. For about 10 c.c. of liquid bromine, 8–9 c.c. of CNCl were taken. After about 12 hours the liquid mixture of bromine and cyanogen chloride solidified to short needle-shaped crystals. The reaction was allowed to continue for five days more.

After this period, the excess of bromine was removed by passing a current of dry air through the apparatus and then through strong alkali. The alkali was tested in the end and found to contain no cyanogen compound. The solid residue was then treated with pure dry chloroform, in which almost the whole of it dissolved. The solution was filtered and the chloroform distilled off, when a crystalline product was formed. This was re-dissolved in chloroform and crystallised, when shining plates were obtained. Re-crystallisation from petroleum ether (60–80°) gave feather-shaped crystals.

This substance contains Carbon, Nitrogen, Chlorine and Bromine. It melts at 160–61° to a colourless liquid which slowly volatilises as the temperature is raised. It sublimes above 100°. It dissolves in ether, carbon disulphide, carbon tetrachloride, petroleum ether and very readily in chloroform, benzene, and acetone. Alcohol decomposes it with the formation of cyanuric acid. It is insoluble in cold water, but dissolves in hot water. Heated with water at 100–20°, cyanuric acid, HCl and HBr are formed. The substance has a strong, pungent, and irritating odour causing tears in the eyes.

The carbon was estimated by the usual method, and the nitrogen by Dumas method. The total halide was estimated by Piria and Schiff's method, and thence the two halogens were estimated separately by Moser and Miksch method of heating the combined silver halides with pure dry ammonium bromide (to convert the chloride into bromide). On analysis the substance was found to have the composition, $\text{Cl} = 47.4\%$, $\text{Br} = 12.85\%$, $\text{N} = 21.43\%$ and $\text{C} = 18.31\%$. From the percentage composition, the calculated formula comes to $\text{C}_5\text{N}_4\text{Cl}_4\text{Br}$ with a molecular weight of 597. But

the molecular weight determined by the cryoscopic method using benzene as the solvent comes to only 206

0.2298 gm. of substance dissolved in 24.8310 gm of benzene gave a depression of 0.225° C. (Mol Weight = 205.6)

0.2477 gm of substance dissolved in 23.9520 gm. of benzene gave a depression of 0.251° C. (Mol Weight = 206).

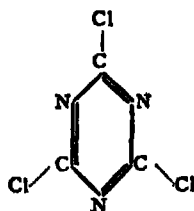
The melting point of substance, however, remains unchanged when crystallised from acetone and carbon tetrachloride and also after subliming

It is probable the substance is a double compound of two molecules of cyanuric chloride, $C_3N_3Cl_3$, and one molecule of monobromo cyanuric chloride, $C_3N_3Cl_2Br$ (see below), which dissociates in benzene into two molecules of $C_3N_3Cl_3$ and one of $C_3N_3Cl_2Br$. This will explain the observed molecular weight (206) in benzene which is nearly one-third the theoretical (597). It is further proved that the substance is a definite compound from the melting point determinations of mixtures of the two compounds, $C_3N_3Cl_3$ and $C_3N_3Cl_2Br$. For, the melting points of mixtures of $C_3N_3Cl_3$ and $C_3N_3Cl_2Br$ mixed in proportions slightly higher and lower than the theoretical ratio 2 : 1 were lower than the m.p. (160°) of the substance ($C_9N_9Cl_6Br$).

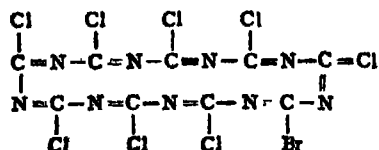
m.p. of a mixture of 0.0241 gm. (70.87%) of $C_3N_3Cl_3$ and 0.0099 gm (29.13%) of $C_3N_3Cl_2Br$ was 156° C

m.p. of a mixture of 0.01103 gm (48.52%) of $C_3N_3Cl_3$ and 0.0117 gm (51.48%) of $C_3N_3Cl_2Br$ was 150° C

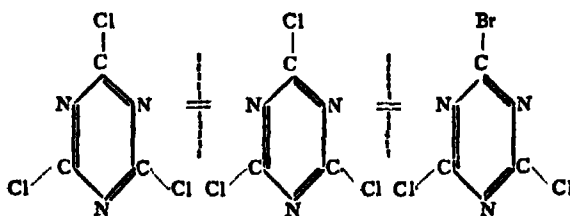
Cyanuric chloride is given a cyclic ring structure as 2 · 4 · 6 · trichloro 1 · 3 · 5 · triazin (Chattaway, 1902)



In a similar manner the constitution of $C_9N_9Cl_6Br$ can be expressed either as



or



The second formula can easily account for the observed dissociation of the compound into three simple molecules in benzene

II Action of Hydrobromic Acid on Cyanuric Chloride

By the action of aqueous hydriodic acid (57%, constant boiling point acid) on cyanuric chloride in the cold, Klason (1886) observed that besides cyanuric iodide, the compound monochloro cyanuric iodide, $C_3N_3I_2Cl$, was also formed as an intermediate product. This was obtained as white feathery crystals by heating the cyanuric iodide formed at about 360° . So it was expected that by a similar treatment of cyanuric chloride with hydrobromic acid (47% constant boiling point acid) the corresponding bromo compound could be obtained. But instead of the bromo compound $C_3N_3Br_2Cl$, only $C_3N_3Cl_2Br$ was obtained.

Experimental

Cyanuric chloride was prepared according to the methods of Klason (1886) and Fries (1886).

Into a flask containing pure dry chloroform, chlorine was passed until saturation. Then chlorine and hydrogen cyanide were both passed simultaneously, keeping the chlorine always in excess and applying strong cooling throughout the experiment. After 12 hours the flask was fitted with a condenser and refluxed until the excess of chlorine, HCl and the unpolymerised CNCl had all escaped. Then the chloroform was distilled off, when a residue of long needle-shaped crystals was got. The product was recrystallised from petroleum ether and dried in a desiccator.

To about a gram of the pulverised cyanuric chloride about 6–8 c.c. of 47% hydrobromic acid were added and constantly stirred. After every three hours, the acid was removed by decantation, fresh acid added and again stirred constantly. The reaction was thus continued for 24 hours. Then it was filtered, washed and dried in a desiccator. The dried product was heated up to 150° when prismatic crystals sublimed. After resubliming it was used for analysis.

This substance contains Carbon, Nitrogen, Chlorine and Bromine. Most of it sublimes below 200°, only a little melts at 210° which slowly volatilises as the temperature is raised further. It dissolves in all the usual organic solvents. Alcohol decomposes it with the formation of cyanuric acid. It is insoluble in cold water, but when heated with water at 120°, cyanuric acid, HCl and HBr are formed.

On analysis the substance is found to have the composition Cl = 30.4%, Br = 34.31%, and N = 18.22%, $C_3N_3Cl_2Br$ requires Cl = 30.98%, Br = 34.92%, and N = 18.37%.

The m.p. of substance remains unchanged when crystallised from chloroform.

The non-volatile residue left behind on heating the washed and dried product of the reaction of hydrobromic acid on cyanuric chloride, also contained carbon, nitrogen, chlorine and bromine. The quantity of substance available was too small for analysis. It did not melt nor sublime upto 280° C.

Further work is in progress.

The author is deeply indebted to late Professor Edward Barnes under whose direction and guidance the work was carried out.

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SPREADING COEFFICIENTS OF NEKAL BX SOLUTIONS

BY M R BHIMASENA RAO AND K S GURURAJA DOSS

(Department of Chemistry, Central College, Bangalore, University of Mysore)

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Introduction

WETTING agents are being extensively used in several of the processes of the textile industry such as kier boiling, dyeing and finishing. The wetting agents bring about thorough wetting and thereby ensure uniformity in the treatment of fabrics. They also accelerate the penetration of liquids into the fabric and thereby increase the speed of operation. A large number of wetting agents having varying degrees of efficiency are now commercially available.

The evaluation of wetting agents is of great importance to the producer as well as the consumer. Several methods are available. Most of the methods however are of a semi-quantitative character. Though they are useful for industrial purposes, they fail to give an exact measure of the wetting property. Theoretically, the determination of the spreading coefficient of the wetting agent solution on the grey yarn should give a precise idea of the wetting power. But, the measurement of this quantity is beset with many difficulties since the system involves solids. Irreproducible kinetic effects, complications due to the roughness of the surface,¹ and friction effects at the meniscus render difficult an accurate determination of the contact angles in such systems. It is therefore preferable to find out the spreading coefficients of wetting agent solutions on a hydrophobic liquid such as a mineral oil and assess the wetting properties.

Cupples² has determined the spreading coefficients by measuring the surface tension of the oil γ_o , surface tension of the aqueous solution γ_w and the interfacial tension γ_{wo} of the oil-aqueous solution interface. The spreading coefficient for water on oil is given by the equation

$$S_{wo} = \gamma_o - \gamma_w - \gamma_{wo}.$$

The interfacial tension values obtained by the ring method are rendered uncertain owing to the frequent occurrence of finite contact angles. We have therefore adopted the free lens technique of Langmuir³ for measuring

the spreading coefficients of nekal BX solutions. The method consists in measuring the diameters of oil lenses formed from known amounts of oil. If V is the volume of oil employed and R is the radius of the lens formed, one can get the value of t_{∞} by plotting the values of $\frac{V}{\pi R^2}$ against $\frac{1}{R}$ and extrapolating to $\frac{1}{R} = 0$.

Experimental

Purification of materials—The nekal BX (sodium dialkyl naphthalene sulphonate) used was a purified specimen prepared from the commercial sample by the following method.⁴ 25 g of dry commercial quality nekal BX were dissolved in 250 c c of alcohol. The solution was allowed to stand overnight in a tall cylinder. The clear supernatant liquid was filtered and the filtrate was concentrated and finally evaporated to dryness. The residue was dried in a hot air oven at 100° C for 3 to 4 hours. The material was powdered and bottled while still hot. The paraffin oil used in these investigations was Evan's "Liquid Paraffin". It was used without further purification as it was found to have the following characteristics. It did not spread on water but formed a lens. It did not develop any surface pressure as indicated by the surface pressure balance and it did not give rise to any appreciable surface film when put on water.

Apparatus

It is to be pointed out that the systems dealt with in this paper are those which exhibit a variation of the surface properties with time.⁴ In order to get comparable and reproducible results, it is necessary to work with surfaces of definite age. In order to enable this, a special shallow glass trough $2' \times 1\frac{1}{2}'$ was constructed by fixing a beading of $\frac{1}{4}"$ glass strips, on a $\frac{1}{4}"$ glass plate by means of a high grade paraffin wax. The edges of the trough were paraffined so that the surface of solutions in the trough could be swept by barriers as in surface film work. Paraffined glass strips were used as barriers. The paraffin oil lenses were photographed from above, using a double extension camera with a Ziess Tessar f/4.5 lens of focal length 13.5 cm stopped down to f/8. Exposure of $1/5$ to $1/2$ second was given. The paraffin oil lens was illuminated from the bottom by means of a 100 watt electric lamp. A sheet of ground glass was interposed between the oil lens and the lamp. As the paraffin oil has a higher refractive index than water, it can easily be shown that the light from the extended source under the conditions of our experiments gets refracted in such a way that the boundary of the oil lens comes out very sharp in the photograph. Distance between the object and the camera was

about 22" and the distance between the lens and the source of light was 24". To find the relationship between the size of the object and the size of the image, an accurate glass scale was photographed from the same distance. An examination of the photograph of the scale showed that the errors due to spherical aberration were negligible. The sensitive material used was Ilford H P. 2 plates and they were hardened during development.

Procedure—The trough was completely filled with the solution. The surface was then cleared with paraffined barriers. The surface tension of the solution at 11, 13 and 15 minutes after clearing were determined by the ring method using Du Nouy tensiometer in its modified form⁴. In calculating the surface tension the corrections of Harkins and Jordan⁶ have been applied. The values obtained are given in Table II and Fig. 1.

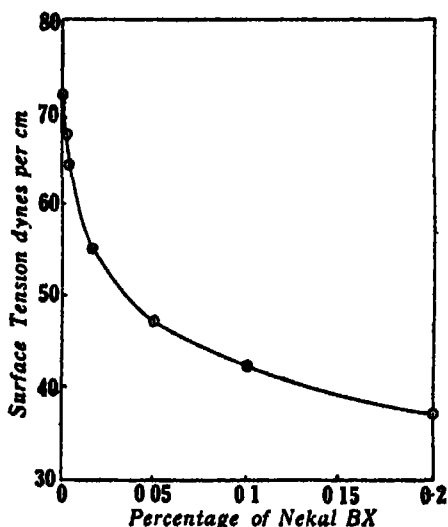


FIG. 1

Surface Tension of Nekal BX Solutions (age of Surface 11 minutes)

Before photographing, the surface was cleared once again and immediately a known weight of paraffin oil was added. Eleven minutes after clearing, the oil lens was photographed. The diameter of the lens on the negative was measured correct to 0.001 cm using a travelling microscope and taking the mean of 2 to 4 even diameters. The work was done in a room free from draughts and at a temperature of $27.5^{\circ} \pm 1.0^{\circ} \text{C}$.

The surface tension of the paraffin oil was determined by the maximum bubble pressure technique as developed in this laboratory⁴.

The values of $\frac{V}{\pi R^2}$, $\frac{1}{R}$, and t_{∞} (extrapolated) obtained in the several systems examined, are given in Table I

The values of the spreading coefficient of oil on water can be calculated by the equation

$$S_{ow} = - \frac{g \rho_2 (\rho_1 - \rho_2) t_{\infty}^2}{2 \rho_1}$$

where g is the acceleration due to gravity, ρ_1 the density of water and ρ_2 the density of the paraffin oil used (0.885)

From these values the spreading coefficient of water on oil is calculated by the equation

$$S_{wo} = S_{ow} - 2 \{ \gamma_w - \gamma_o \}$$

where γ_w and γ_o are the surface tensions of the aqueous solution and paraffin oil respectively

The interfacial tension γ_{wo} of the aqueous solution-oil interface has been calculated by the equation

$$\gamma_{wo} = -S_{ow} + \gamma_w - \gamma_o$$

The adhesion tension of water against oil is given by the equation

$$A_{wo} = \gamma_o - \gamma_{wo}$$

The values of all these quantities for nekcal BX solutions of different concentrations are given in Table II and Figs 2 to 5

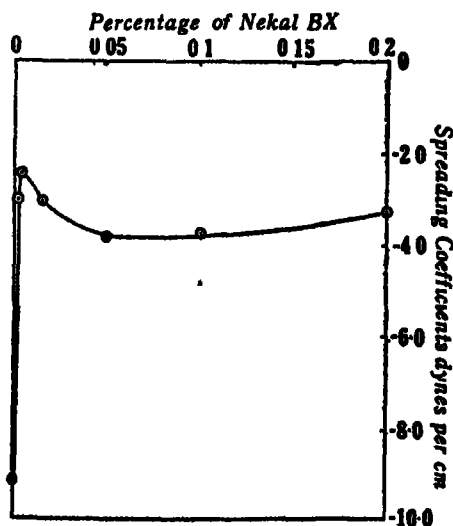


FIG. 2

Spreading Coefficients of Paraffin Oil on Nekal BX Solutions.

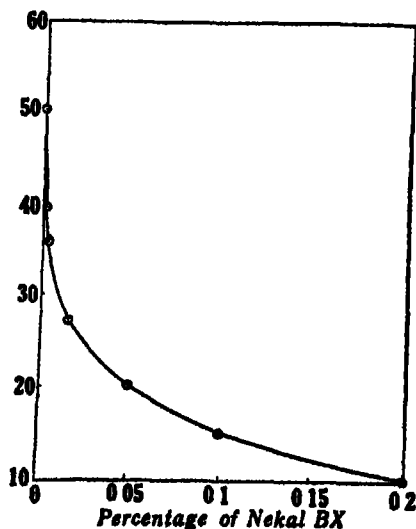


FIG. 3

Interfacial Tension of Paraffin Oil Nekal BX Solution Interface

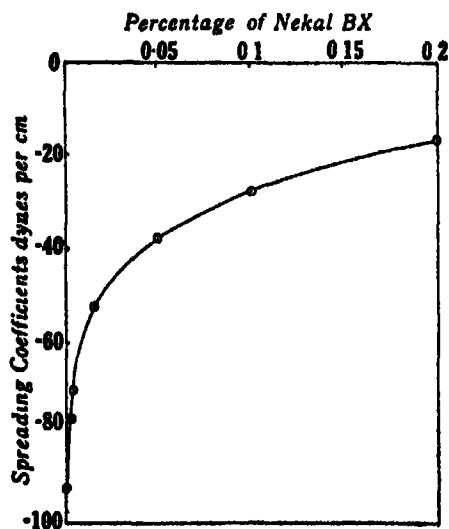


FIG. 4

Spreading Coefficients of Nekal BX
Solutions on Paraffin Oil

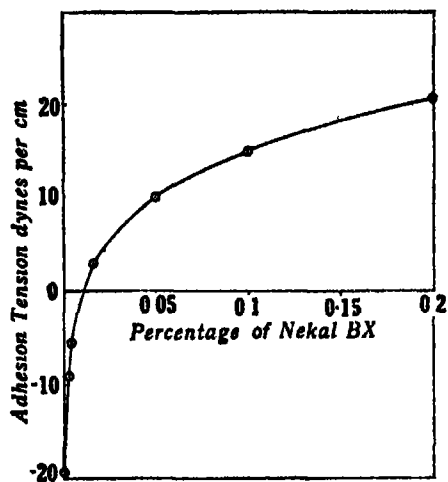


FIG. 5

Adhesion Tension of Nekal BX Solutions
(Age in Interfaces 11 minutes)

TABLE I

Concentration of Nekal BX 0.00%		Concentration of Nekal BX 0.0025%		Concentration of Nekal BX 0.005%		Concentration of Nekal BX 0.017%	
1/R	$\frac{V}{\pi R^2}$	1/R	$\frac{V}{\pi R^2}$	1/R	$\frac{V}{\pi R^2}$	1/R	$\frac{V}{\pi R^2}$
0.171	0.427	0.161	0.151	0.190	0.185	0.175	0.214
0.160	0.427	0.156	0.156	0.153	0.194	0.147	0.226
0.156	0.428	0.118	0.179	0.122	0.153	0.132	0.223
0.102	0.430	0.116	0.190	0.111	0.202	0.099	0.235
0.000	0.434*	0.000	0.250*	0.093	0.219	0.091	0.237
				0.000	0.226*	0.000	0.262*

* Extrapolated.

TABLE I (Contd)

Concentration of Nekal BX 0.05%		Concentration of Nekal BX 0.1%		Concentration of Nekal BX 0.2%	
1/R	$\frac{V}{\pi R^3}$	1/R	$\frac{V}{\pi R^3}$	1/R	$\frac{V}{\pi R^3}$
0.177	0.227	0.183	0.239	0.183	0.256
0.160	0.236	0.151	0.246	0.139	0.257
0.139	0.245	0.136	0.243	0.111	0.258
0.112	0.244	0.105	0.256	0.000	0.262*
0.092	0.254	0.094	0.261		
0.000	0.282*	0.000	0.278*		

* Extrapolated.

TABLE II

Concentration of Nekal BX weight %	γ_{wo} dynes/cm	S_{ow} dynes/cm	γ_{wo} dynes/cm	S_{wo} dynes/cm	A_{wo} dynes/cm
0.0000	72.0	-9.10	50.3	-91.5	-19.5
0.0025	67.6	-3.00	39.8	-76.6	-9.0
0.005	64.6	-2.46	36.3	-70.1	-5.5
0.017	55.5	-3.31	28.0	-52.7	+2.8
0.05	47.9	-3.84	20.9	-38.0	+9.9
0.1	42.9	-3.73	15.8	-27.9	+15.0
0.2	37.7	-3.30	10.2	-17.1	+20.6

Discussion

1. *Spreading coefficients of oil on aqueous solutions* — A glance at Fig. 2 shows that the presence of nekcal BX to the extent of 0.005% increases tremendously the spreading of paraffin oil. Further increase in concentration does not considerably affect the spreading though the minimum in the curve is followed by a small flat maximum. The first sudden increase in the spreading is presumably due to the solute molecules accumulating more easily at the oil-aqueous solution interface than at the air-aqueous solution interface. At higher concentrations, the solute accumulates to nearly the same extent

at both the interfaces. It may therefore be concluded that small quantities of nekal BX very much improve the spreading properties of oils on polar surfaces. This fact appears to be of great interest in lubrication problems.

2 Spreading coefficients of aqueous solutions on oil and the adhesion tensions—The spreading coefficients of aqueous solutions become less and less negative as the concentration of nekal BX is increased (Fig. 4). The wetting power of the solutions is therefore increased by raising the concentration of nekal BX. It is however to be noted that the spreading coefficient does not become positive even at the highest concentrations tried. It appears therefore that the process of wetting of the grey yarn by these solutions (assuming that the wetting characteristics of grey yarn and liquid paraffin are similar) is not by spreading but takes place by creeping of the liquid into the capillary spaces. This tendency is determined by the adhesion tension of the aqueous solution against oil which is given by $\gamma_o - \gamma_{wo}$ and not by the spreading coefficients. The values of adhesion tension is negative for water and for dilute solutions and becomes positive only with concentrations higher than 0.0%15 of nekal BX (*vide* Fig. 5).

The adhesion tension of aqueous solution against oil

$$A_{wo} = \gamma_o - \gamma_{wo} = 2\gamma_o - \gamma_w + S_{ow}$$

Since S_{ow} is more or less constant at all concentrations of nekal BX (except with the most dilute solutions) it is clear that the adhesion tension is mainly determined by the value of γ_w . Thus the surface tension lowering may be taken as a rough measure of the wetting power. This conclusion can also be justified on theoretical grounds. A solute which strongly lowers the surface tension of water is strongly adsorbed at the surface. The high adsorption is caused by the presence of hydrophobic portions in the solute molecule. Such a solute can also be expected to be adsorbed at the mineral oil-water interfaces. So the interfacial tension would be low. The adhesion tension $\gamma_o - \gamma_{wo}$ would be correspondingly high. Thus the surface tension lowering would run parallel to the values of the adhesion tension and would therefore be a rough measure of the wetting power.

Summary

The spreading coefficients of paraffin oil on nekal BX solutions have been determined by the floating lens technique of Langmuir. These measurements combined with the surface tension of the aqueous solutions give an exact idea of the wetting characteristics of the solutions. A rough measure of the wetting power is shown to be given by a measurement of the surface tension of the aqueous solution.

It is shown that small quantities of nekal BX greatly improve the spreading qualities of oils on polar surfaces

The spreading coefficients of nekal BX solutions are found to be negative even at the highest concentrations tried. It is therefore suggested that the wetting takes place by penetration and not by spreading. Thus, the adhesion tension of the aqueous solutions against oil gives a more correct measure of the wetting power.

In conclusion, the authors wish to thank Professor B. Sanjiva Rao, for his kind and helpful interest in the work.

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A STUDY OF THE RAMAN EFFECT IN SEVENTEEN OPTICAL GLASSES

BY R. NORRIS

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

RAMAN EFFECT investigations on glass are not very numerous, and further work on the subject is greatly to be desired as our knowledge of the structure of glass is far from being complete at the present time. Amongst the more important investigations in this field are those of Raman (1928), Gross and Romanova (1929), Bhagavantam (1931), Kujumzelis (1935), and Langenberg (1937). Prof. Raman noticed that the spectrum of glass generally consists of diffuse bands and not sharp lines. Gross and Romanova studied two Russian optical glasses, one a crown and the other a flint, as well as amorphous and crystalline quartz and recorded a series of bands in these glasses and in fused quartz, and concluded that these bands correspond roughly to the lines observed in the case of crystalline quartz. They also noted that the bands are more intense with flint than with crown glass.

Bhagavantam studied a series of ten optical glasses from the firm of Schott of Jena. He recorded the presence of a band at $460 \rightarrow 520 \text{ cm}^{-1}$ with all the glasses and of another band at $780 \rightarrow 800$ which occurs with nearly all of them. He also noticed that the feeble band at 1080 observed with the crown glasses is less intense than the $460 \rightarrow 520$ band, and that the two much stronger bands at 1000 and 1080 exhibited by the flint glasses are more intense than the band at $460 \rightarrow 520$, though the latter also gained in intensity in passing from the crown to the flint glasses. Bhagavantam further noticed a band at 640 in a light baryta flint glass, and a band at 650 in a dense boro-silicate crown; the latter also exhibits a band at 340. With some of the glasses a feeble band at 1320 was also observed.

Kujumzelis carried out a systematic study with nineteen optical glasses also from the firm of Schott, as well as with fused quartz and fused boron trioxide. He drew attention to an important feature, namely, that the Raman spectrum of glass includes a continuum stretching from the exciting line towards longer wave-lengths and showing a fairly well-defined limit at about

530 wave numbers from the exciting line. This is traversed, however, by subsidiary bands, especially in the vicinity of its outer edge. All the lead glasses studied by Kujumzelis showed, in addition, a weak band in the 600 region, a somewhat stronger band at about 780, and four bands within the frequency range 900 to 1200, of which the two central ones were the most intense, the positions of these latter shift towards the exciting line with increasing lead content of the glass. Fused silica showed bands at $230 \rightarrow 450$ and a continuum having a limit at 500, bands at $607, 780 \rightarrow 840, 1030 \rightarrow 1090$ and $1160 \rightarrow 1230$. Pure boric oxide glass showed a sharp line at 808. The work of Kujumzelis showed that the spectrum of glass is strongly influenced by its chemical composition, both as regards the position and the intensity of the bands, and especially by the proportion of boric and lead oxides to silica. Langenberg studied twenty-six optical glasses including pure boric oxide glass and fused quartz, all except the last being from the firm of Schott. While confirming the results of Kujumzelis, he attempts to attribute the frequencies of the various observed bands with the vibration frequencies of the several chemical components in the glass, as for instance to the SiO_4 -ion in the silicate glasses and to the BO_3 -ion in the borate glasses.

Reference may be made also to the recent work of Matossi and Bluschke (1938), who have studied the infra-red reflection spectra of about 23 glasses of different compositions. All the silicate glasses show broad bands of which the two stronger have their maxima at about 9μ and between 22 to 23μ respectively. Weaker bands are also observed at $8.8\mu, 12.8\mu$, and 20.9μ for fused quartz glass, at 7μ and 14.8μ for silica-barium glasses with boron content, and at $7\mu, 11.5\mu$ and 14.8μ for borate glasses containing lead.

The present paper records the results of a study of the Raman spectra of seventeen optical glasses, manufactured by the firm of Schott at Jena.

2 Specimens Studied

Table I gives the list of the glasses studied, as also their composition and density furnished by the manufacturers. They were all in the form of rectangular slabs ($3 \times 3 \times 2$ c.c.) with all except two of their end faces polished. These were the same specimens with which R. S. Krishnan (1936) carried out in this Laboratory his investigation on "Scattering of Light in Optical Glasses". The refractive indices of the specimens given in Table I are the values as measured by him with a Pulfrich refractometer. The Raman spectrum of crystalline quartz in the form of a cylinder of length 5 cm and diameter 2.5 cm. has also been recorded for purpose of comparison.

TABLE I

Serial Number	Melting Number	Glass contains traces of Al_2O_3 , Fe_2O_3 , As_2O_3 and Oxides in		Density	Refractive index μ_n
		more than 10%	less than 10%		
1	25188	SiO_2 , B_2O_3 , Al_2O_3 , K_2O	Na_2O , F	2.3	1.4670
2	18415	SiO_2 , B_2O_3 , K_2O	Al_2O_3	2.3	1.4925
3	16776	SiO_2 , K_2O	Al_2O_3 , Na_2O , CaO	2.4	1.5022
4	23975	SiO_2 , B_2O_3 , ZnO	Al_2O_3 , Na_2O	2.5	1.5095
5	24906	SiO_2 , B_2O_3	Na_2O , K_2O , BaO	2.5	1.5269
6	22601	SiO_2 , B_2O_3 , Sb_2O_3	Al_2O_3 , Na_2O , K_2O	2.7	1.5294
7	23125	SiO_2 , Na_2O , PbO	ZnO	2.7	1.5370
8	22638	SiO_2 , PbO	Na_2O , K_2O	2.9	1.5449
9	24464	SiO_2 , ZnO, BaO	B_2O_3 , Na_2O , K_2O , PbO	3.1	1.5697
10	19510	SiO_2 , PbO	Na_2O , K_2O	3.2	1.5698
11	23355	SiO_2 , B_2O_3 , BaO	Al_2O_3 , Na_2O	3.3	1.5892
12	20672	SiO_2 , PbO	B_2O_3 , Na_2O , K_2O	3.4	1.5983
13	22986	SiO_2 , BaO, PbO	Na_2O , K_2O , ZnO	3.5	1.6163
14	23441	SiO_2 , PbO	Na_2O , K_2O	3.9	1.6473
15	23497	SiO_2 , BaO, PbO	Na_2O , K_2O , ZnO	3.9	1.6498
16	23850	SiO_2 , PbO	Na_2O , K_2O	4.4	1.7130
17	23590	SiO_2 , PbO	Na_2O , K_2O	5.1	1.7830

3. Experimental Arrangements

All the specimens were investigated with a Fuess glass spectrograph of large light-gathering power. Each of the glass slabs was illuminated by placing the mercury arc near its side and the scattered light was focussed directly on to the slit of the spectrograph. Most of the specimens showed strong fluorescence which masked the Raman spectrum. This disturbance was effectively eliminated by cutting out the 4046 Å region of the mercury arc with a suitable filter, a saturated solution of $NaNO_2$ (sodium nitrite) in water kept in a specially made pyrex glass cell was found to serve the purpose very well. As the glass No. 17 was coloured yellow, no filter was necessary in this case; 4358 Å being the exciting wave-length. Ilford selochrome plates were used. The photographic plates were measured on a micrometer by comparison with the iron arc spectrum taken along with the spectra

on the plates. In the case of the weak and diffuse bands, the measurements were necessarily rough.

The continuum following the exciting line, which will be mentioned in the next section, is shown to be a genuine Raman effect, and not a case of fluorescence by taking the glasses which are not strongly fluorescent and utilising only the 4046 Å line of the mercury arc as the exciting line and cutting out the 4358 Å radiation with a concentrated solution of Iodine in CCl_4 before entry of the light into the glass. The continua are then found to accompany the 4046 Å line, exhibiting the same limit for the frequency shift, while the continua following the 4358 Å line disappear.

4 Results

The Raman spectra obtained in the case of the glasses consist in general of broad and diffuse bands, as will be seen in Plate VII. It is considered advantageous to give the frequency displacements and the intensities of the bands in the form of graphical representations, in Figs 1 and 2; the intensities of the various bands in each case are drawn relative to the most

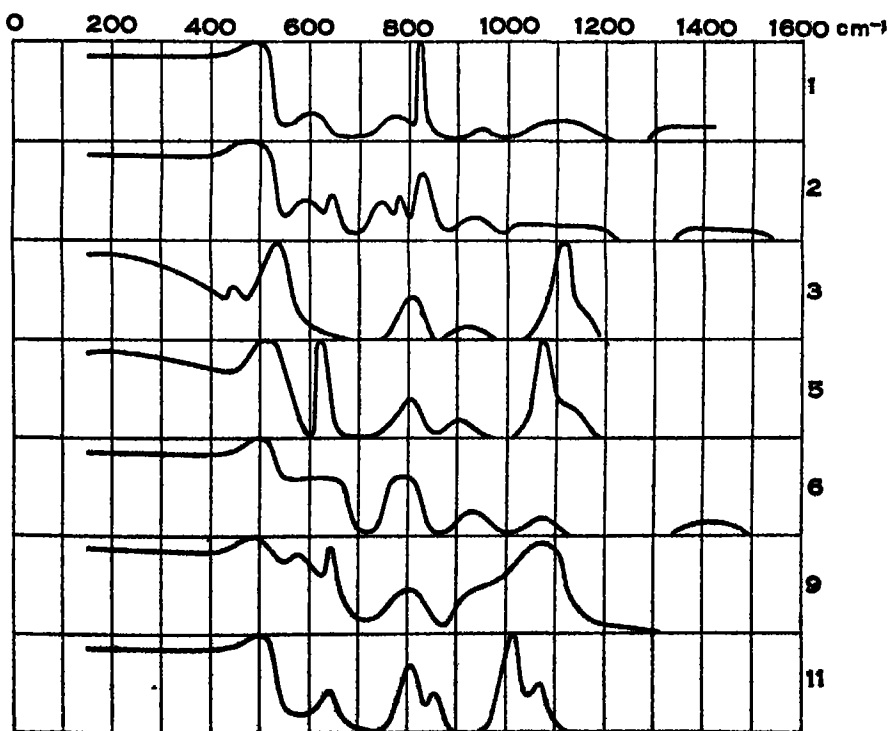


FIG. 1

Graphical Representation of the Raman Effect of Silica Glasses

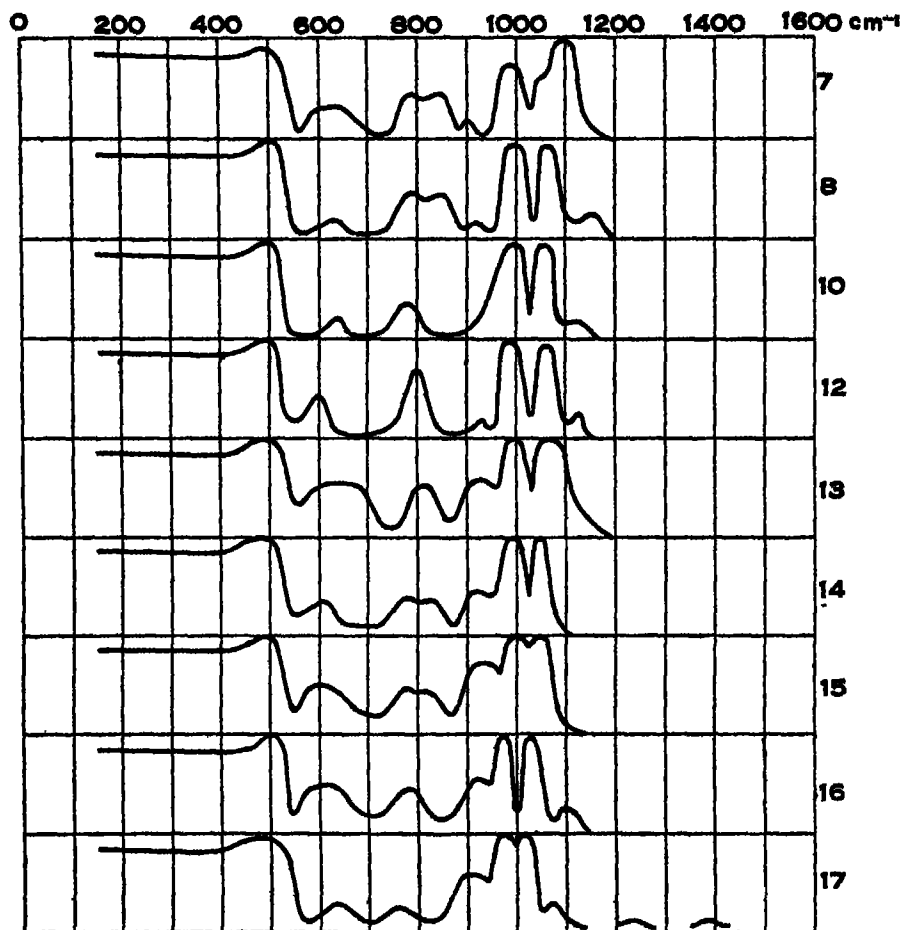


FIG. 2

Graphical Representation of the Raman Effect of Si-Pb Glasses

intense band of that specimen. The actual measurements of the bands are given in Tables II and III. The general characteristics of the Raman spectra are similar for glasses of the same qualitative composition, but vary in detail from glass to glass. As reported by Kujumzelis, each glass exhibits a continuum closely following the exciting line and ending abruptly with a limit at about 530 wave numbers. These continua end with a sharp limit in glasses containing PbO, while they do not end so sharply and are followed by a certain haziness beyond this limit in the other glasses, especially those which do not contain PbO. This can be seen to be so in the case of glasses of Nos. 3, 5, 6, 9 and 11 of the present study. That these continua are due to genuine Raman effect and not due to fluorescence has been demonstrated, as already

TABLE II
Frequency Shifts and Approximate Intensities of the Raman Bands in Silica Glasses

1	2	3	5	6	9	11
- 512 Lt.	- 517 Lt.	- 555 Lt.	- 558 Lt.	- 520 Lt.	- 555 Lt.	- 528 Lt.
434- 512 (v.s.)	447- 517 (v.s.)	450 (f.s.)				495- 528 (s.)
512- 633 (e.w.)	517- 644 (e.w.)	523- 555 (v.s.)	495- 558 (s.)	520- 670 (f.s.)	580 (s.)	
603 (w.)		555- 675 (w.)	634 (v.s.)		640 (sh.)	639 (w.)
722- 816 (e.w.)	768 (w.)	771- 830 (f.s.)	726 (w.)	780- 820 (f.s.)	768- 844 (f.s.)	673 (w.)
816 (sh.)	803- 840 (f.s.)					810 (s.)
931 (w.)	890- 969 (w.)	852- 995 (w.)	904 (w.)	930 (w.)	908-1143 (w.)	845 (f.s.)
1014-1186 (w.)	1012-1240 (e.w.)	1073-1136 (v.s.)	1037-1086 (f.s.)	1070 (w.)	1036-1116 (v.s.)	976-1042 (s.)
		1050-1194 (s.)	1086-1198 (w.)		1150-1300 (e.w.)	1065 (f.s.)
	1350-1670 (e.w.)			1340-1500 (e.w.)		1133 (w.)
						1258-1460 (e.w.)

TABLE III
Frequency Shifts and Approximate Intensities of the Raman Bands in *Sn-Pb Glasses*

7	8	10	12	13	14	15	16	17
- 529 Lt	- 528 Lt.	- 528 Lt	- 526 Lt	- 530 Lt	- 528 Lt	- 531 Lt	- 528 Lt	- 530 Lt
588- 668 (w.)	640 (w.)	632 (w)	603 (w)	593- 702 (f s)	619 (w)	610 (w)	573- 673 (w)	639 (e w)
759- 868 (f.s.)	760- 870 (f s)	781 (f.s)	810 (f s)	772- 843 (f s.)	769- 847 (f s)	754- 802 (f s)	747- 811 (f s)	778 (w)
895 (w)	908 (w)		928 (e w)	897- 961 (s)	894- 946 (f s)	894- 961 (s)	894- 947 (f s)	879- 946 (s)
967-1024 (s.)	978-1017 (v s)	968-1024 (v s.)	964-1017 (v s)	966-1024 (v s)	964-1015 (v s)	969-1019 (v s)	947- 990 (v s)	949- 990 (v s)
1043 (w.)					1019-1062 (v s)	1024-1086 (v s)	1014-1068 (vs)	993-1037 (v s)
1063-1123 (v.s)	1041-1085 (v.s.)	1037-1085 (v.s)	1037-1085 (v s)	1045-1120 (v.s)				
	1177 (w)	1130 (w.)	1131 (w)	1120-1200 (e w)			1100 (e w)	1086 (w)
								1256 (e.w)
								1383 (e w)

Lt., Limit, e.w, extremely weak, w, weak, f.s, fairly strong, v s, very strong, s, strong, sh, sharp

mentioned, by the use of filters. In the sufficiently well exposed plates the continua also appear on the shorter wavelength side of the exciting line, the limiting frequency shift being the same as for the one on the longer wavelength side. In the glass No 1, which contains both boric oxide and fluorine the band at 800 is sharp and intense, and the continuum stretching upto about 500 is strong, while the other bands are relatively weak and diffuse. The same features are also observed in glass 2, which is of similar composition but for the omission of fluorine, except that the 800 band is not now so marked. A comparison between the glasses 3 and 5 is specially interesting, the latter containing boric oxide and the former not. In the silica-alkali glass, the continuum is weak, but a band at 540 is strong and well defined, while in the glass containing boric oxide, the continuum is stronger but the band at 520 is not so well defined. On the other hand, in glass 5, the band at 634 is strong, while in glass 3, it is not noticeable. In both glasses the band in the 1000–1200 region is strong, but more so in glass 3. Glass 4 was too strongly fluorescent to give any useful results. Glass 11 which is a heavy one containing barium but no lead shows a definite shift of the band at 1000 towards the exciting line which is very significant in view of the analogous results shown by the lead glasses, which we shall comment upon. The Si-Pb glasses exhibit a characteristic Raman spectrum, having an intense continuum with a sharp limit, this limit remaining the same for all the glasses of the series irrespective of lead content, as also two weak and diffuse bands at 600 and 800 and two very prominent bands in the 950→1100 region, with weaker bands on either side of them. Glass 7 appears also to exhibit a weak band at about 1050 between the two stronger bands. It is noteworthy, as has already been observed by Kujumzelis, that with increasing lead content the two intense bands in the 950→1100 region are gradually displaced towards the exciting radiation, while at the same time they approach nearer each other. The presence of BaO in the glasses has the effect of making these two strong bands more intense, as also to cause them to approach each other and shift towards the exciting line but to a lesser extent than for lead glasses, it appears also to result in an enhancement of the intensity of the bands at 600, 800 and of the weak one at 930.

The interpretation of these results will be discussed in a later communication.

In conclusion, the author takes this opportunity to thank Prof Sir C V Raman for his keen interest in this work.

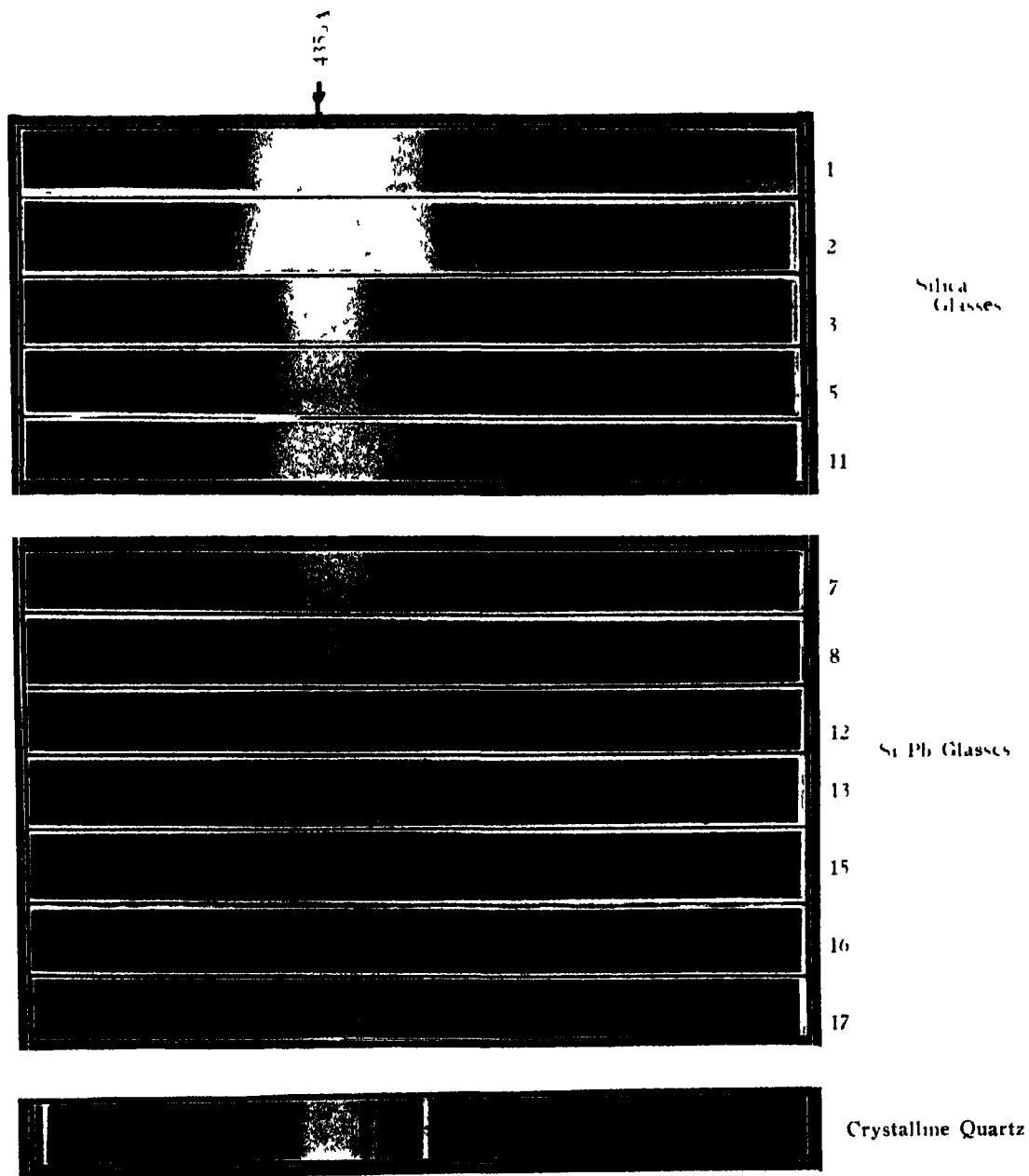
Summary

The Raman spectra of a representative collection of seventeen optical glasses of varying composition and density were investigated. The observed

results are given in the tables as well as in the form of graphical representations and the spectra are also reproduced in the Plate, and their relation to chemical composition is pointed out. A resumé of the results of the previous investigators in this field is also given. The continua that follow the exciting line in the spectra are shown to be due to a genuine Raman effect and not a case of fluorescence. The work broadly confirms the experimental results of Kujumzelis. Important features, as for instance the influence of barium and lead oxides on the spectra are also emphasised. The effect of the presence of boric and lead oxides on the distribution of intensity on the continuum is a noteworthy feature brought out by the present investigation.

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THE GRAVITATIONAL EQUATIONS OF MOTION IN RELATIVITY

BY V V NARLIKAR

(From the Department of Mathematics, Benares Hindu University)

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§1 IN a recent paper, which will here be referred to as E I H, Einstein, Infeld and Hoffmann¹ have given a new relativity theory of gravitation. It marks an important departure from the well-known general theory which the authors describe as classical relativity. The essence of the new theory lies in its possession of the three ideal features which were the desiderata of the earlier theory. Einstein^{2,3,4} has stated them in a number of publications during the last six years or so. They may be expressed briefly as follows: (A) Field equations should give both matter and motion, (B) the geodesic postulate⁵ being redundant should have no place in the field theory, (C) the duality of the field energy and matter^{4,6} being unsatisfactory the problem of gravitating matter should be solved without the use of an extraneous energy-momentum tensor such as $T_{\mu\nu}$. The three ideas are interconnected. It is essential to understand them if the significance of the results arrived at in this paper is to be grasped.

A logical working out of these ideas which covers the entire domain of phenomena of general relativity is a definite advance over the latter theory inasmuch as a greater economy and generality are achieved in the choice of the number and nature of the basic postulates and hypotheses. The solution of the problem of n bodies given in E I H is such a logical working out of the new ideas. Thus the gravitational equations of motion are obtained purely from the field equations,

$$G_{\mu\nu} = 0, \quad (1)$$

the solution being subject to the condition that the space-time frame is flat at infinity. This method must be distinguished from the earlier and unsatisfactory attempts of de Sitter, Levi Civita and Eddington and Clark⁷ who had to use not only the more complicated equations,

$$G_{\mu\nu} - \frac{1}{2} G g_{\mu\nu} = -k T_{\mu\nu}, \quad (2)$$

but the equations of geodesics also, viz.,

$$\frac{d^2 x^\mu}{ds^2} + \Gamma_{\alpha\beta}^\mu \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0 \quad (3)$$

(The equations so far written appear in the usual notation and therefore no attempt will be made to define the various symbols) The latter procedure is in contravention of Einstein's ideas and it introduces the difficulties of infinite self-energy which are quite common in the quantum theories of fundamental particles

§2 The problem⁵ that we take up is this Following the procedure of E I H one gets as a solution of (1),

$$g_{\mu\nu} = g_{\mu\nu}(m_1, m_2, \dots, m_n) \quad (4)$$

and the $3n$ equations of motion of the particles are obtained, those of m_1 being, say,

$$f^m(m_1, m_2, \dots, m_n) = 0 \quad m = 1, 2, 3 \quad (5)$$

For the line-element given by (4) we have the equations of geodesics which with the time co-ordinate τ as the independent variable can be cast into the form

$$g^m(m_1, m_2, \dots, m_n) = 0 \quad m = 1, 2, 3 \quad (6)$$

If we put $m_1 = 0$ in (5)

$$f^m(0, m_2, \dots, m_n) = 0 \quad (7)$$

are the equations of a particle of zero mass in the field of $n - 1$ particles If, however, the geodesic postulate were valid the required equations would be

$$g^m(0, m_2, \dots, m_n) = 0 \quad (8)$$

In general the two sets of equations, (7) and (8), would not be identical since the geodesic postulate has been weeded out as extraneous and unnecessary in the treatment of E I H It is interesting to find out therefore at what stage the new equations of motion deviate from the geodesic postulate When the necessary calculations are carried out we discover the surprising result that the equations (7) and (8) are identical in form and content to the second order of masses, that is, as far as the right-hand side of (5) is computed in E I H, in the two-body problem Thus the geodesic postulate is found to be consistent with the equations of motion of the new theory at least over the first two phases of approximation What will happen at higher approximations cannot be foretold without doing very lengthy calculations In what follows the consistency will be established and an explanation will also be provided how it arises

§3 Consider* the flat Galilean space given by the matrices $\eta_{\mu\nu}$ and $\eta_{\mu\nu}$ whose principal diagonals alone have non-zero members, being 1, -1,

* A full exposition of E I H. will be found in the author's paper referred to as (6)

-1, -1 in order x^0 is the time co-ordinate and x^1, x^2, x^3 are the space co-ordinates. Throughout the rest of the paper the Greek indices such as μ and ν refer to both space and time and run over 0, 1, 2, 3 while the Latin indices such as m and n take on only the spatial values 1, 2, 3. The dummy-suffix convention is resorted to wherever possible to indicate summation. Thus for the Galilean space

$$ds^2 = \eta_{\mu\nu} dx^\mu dx^\nu = (dx^0)^2 - (dx^1)^2 - (dx^2)^2 - (dx^3)^2 \quad (9)$$

Since the velocity of light is taken as unity in this it is convenient to use an auxiliary time co-ordinate τ so that

$$\frac{\partial \phi}{\partial x^0} = \lambda \frac{\partial \phi}{\partial \tau}, \quad (10)$$

where ϕ is a differentiable function of x^μ and λ is a small parameter. This makes $\partial \phi / \partial \tau$ of the same order as $\partial \phi / \partial x^m$.

The line-element of Einstein's¹ solution of the problem of two bodies of masses m_1 and m_2 runs as follows

$$ds^2 = g_{\mu\nu} dx^\mu dx^\nu = (\eta_{\mu\nu} + h_{\mu\nu}) dx^\mu dx^\nu \quad (11)$$

where,

$$h_{00} = \lambda^2 \left[-\frac{2m_1}{r_1} - \frac{2m_2}{r_2} \right] + \lambda^4 \left[-m_1 \frac{\partial^2 r_1}{\partial \tau^2} - m_2 \frac{\partial^2 r_2}{\partial \tau^2} + 2 \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right)^2 \right. \\ \left. + \left(\frac{1}{2} \dot{\eta}^s \dot{\eta}^s - \frac{m^2}{r_{12}} \right) \left(-\frac{2m_1}{r_1} \right) + \left(\frac{1}{2} \xi^s \xi^s - \frac{m_1}{r_{12}} \right) \left(-\frac{2m_2}{r_2} \right) \right] + O(\lambda^6), \quad (12)$$

$$h_{0m} = \lambda^3 \left(\frac{4m_1}{r_1} \dot{\eta}^m + \frac{4m_2}{r_2} \xi^m \right) + O(\lambda^5), \quad (13)$$

$$h_{mn} = -\lambda^2 \delta_{mn} \left(\frac{2m_1}{r_1} + \frac{2m_2}{r_2} \right) + O(\lambda^4) \quad (14)$$

In the above expressions δ_{mn} stands for the Kronecker delta so that

$$\left. \begin{aligned} \delta_{mn} &= 0, \quad m \neq n \\ &= 1, \quad m = n \end{aligned} \right\} \quad (15)$$

Also

$$\left. \begin{aligned} r_{12}^2 &= (\eta^m - \xi^m)(\eta^m - \xi^m), \\ r_1^2 &= (x^m - \eta^m)(x^m - \eta^m), \\ r_2^2 &= (x^m - \xi^m)(x^m - \xi^m), \end{aligned} \right\} \quad (16)$$

η^m, ξ^m being the spatial co-ordinates of m_1 and m_2 respectively at time τ . An overhead dot denotes a differentiation with regard to τ . The metric (11)

satisfies the field equations (1) only if the six equations of motion for m_1 and m_2 are satisfied. Those for m_1 run as follows †

$$\begin{aligned} \eta^m - m_2 \frac{\partial (1/r_{12})}{\partial \eta^m} &= m_2 \lambda^2 \left\{ [\eta^s \dot{\eta}^s + \frac{4}{3} \xi^s \xi^s - 4 \eta^s \xi^s - \frac{4m_2}{r_{12}} - \frac{5m_1}{r_{12}}] \frac{\partial}{\partial \eta^m} (1/r_{12}) \right. \\ &\quad + [4 \dot{\eta}^s (\xi^m - \dot{\eta}^m) + 3 \dot{\eta}^m \xi^s - 4 \xi^m \xi^s] \frac{\partial}{\partial \eta^s} (1/r_{12}) \\ &\quad \left. + \frac{1}{2} \frac{\partial^2 r_{12}}{\partial \eta^m \partial \eta^s \partial \eta^t} \xi^s \xi^t \right\} \quad m = 1, 2, 3. \end{aligned} \quad (17)$$

The equations of m_2 can be similarly written down by interchanging the mass-constants as also the co-ordinates. The constant λ^2 on the right-hand side may be absorbed either in m_1 and m_2 which are just constants of integration or by reverting to x° as the independent variable in place of τ .

The equations of a geodesic are given by

$$\frac{d^2 x^\mu}{ds^2} + \Gamma_{\alpha\beta}^\mu \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0. \quad (18)$$

Taking τ as the independent variable we restate (18) as

$$\lambda^2 \ddot{x}^m + \lambda^2 \dot{x}^m (d^2 \tau / ds^2) / (d\tau / ds)^2 + \Gamma_{\alpha\beta}^m + 2\lambda \dot{x}^\alpha \Gamma_{\alpha\beta}^m + \lambda^2 x^\beta \dot{x}^\gamma \Gamma_{\beta\gamma}^m = 0 \quad (19)$$

The three equations (19) together with the equation supplied by the metric, viz.,

$$\lambda^2 (ds/d\tau)^2 = g_{00} + 2 g_{0\alpha} \dot{x}^\alpha + \lambda^2 g_{\alpha\beta} x^\beta \dot{x}^\gamma \quad (20)$$

are equivalent to the four equations (18). From (19) and (20) one concludes that

$$\begin{aligned} 0 &= \lambda^2 \ddot{x}^m + \Gamma_{\alpha\beta}^m + 2\lambda \dot{x}^\alpha \Gamma_{\alpha\beta}^m + \lambda^2 x^\beta \dot{x}^\gamma \Gamma_{\beta\gamma}^m \\ &\quad - \lambda^2 \dot{x}^m \cdot \frac{1}{2} \frac{d}{d\tau} \log (g_{00} + 2 g_{0\alpha} \dot{x}^\alpha + \lambda^2 g_{\alpha\beta} \dot{x}^\beta \dot{x}^\gamma) \end{aligned} \quad (21)$$

For the evaluation of the various terms in the last equation it is enough to note that

$$g^{\mu\nu} = \eta^{\mu\nu} + h^{\mu\nu} \quad (22)$$

where

$$h^{00} = \lambda^2 \left(\frac{2m_1}{r_1} + \frac{2m_2}{r_2} \right) + O(\lambda^4), \quad (23)$$

$$h^{0\alpha} = \lambda^2 \left(\frac{4m_1}{r_1} \dot{\eta}^\alpha + \frac{4m_2}{r_2} \dot{\xi}^\alpha \right) + O(\lambda^6), \quad (24)$$

$$h^{\alpha\beta} = \delta_{\alpha\beta} \lambda^2 \left(\frac{2m_1}{r_1} + \frac{2m_2}{r_2} \right) + O(\lambda^4) \quad (25)$$

† The notation is the same as that in Reference (6), the overhead indices being dropped for suffixes. (17) is the same as (11.67) of Reference (6).

Thus

$$\begin{aligned}
 \Gamma_{\alpha\alpha}^m &= \frac{1}{2} g^{m\mu} \left[\frac{\partial h_{\mu 0}}{\partial x^0} + \frac{\partial h_{\mu 0}}{\partial x^0} - \frac{\partial h_{00}}{\partial x^\mu} \right] \\
 &= \lambda^2 \frac{\partial}{\partial x^m} \left[-\frac{m_1}{r_1} - \frac{m_2}{r_2} \right] \\
 &+ \lambda^4 \left\{ -\frac{\partial}{\partial \tau} \left[\frac{4m_1}{r_1} \eta^m + \frac{4m_2}{r_2} \xi^m \right] + 2 \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \right. \\
 &\quad + \frac{1}{2} \frac{\partial}{\partial x^m} \left[-m_1 \frac{\partial^2 r_1}{\partial \tau^2} - m_2 \frac{\partial^2 r_2}{\partial \tau^2} + 2 \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right)^2 \right. \\
 &\quad \left. \left. - \frac{2m_1}{r_1} \left(\frac{1}{2} \eta^s \eta^s - \frac{m_2}{r_{12}} \right) - \frac{2m_2}{r_2} \left(\frac{1}{2} \xi^s \xi^s - \frac{m_1}{r_{12}} \right) \right] \right\} \\
 &+ 0 (\lambda^6), \tag{26}
 \end{aligned}$$

$$\begin{aligned}
 2 \lambda \dot{x}^n \Gamma_{\alpha\alpha}^m &= 2 \lambda \dot{x}^n \frac{1}{2} g^{m\mu} \left(\frac{\partial h_{\mu 0}}{\partial x^0} + \frac{\partial h_{\mu 0}}{\partial x^0} - \frac{\partial h_{00}}{\partial x^\mu} \right) \\
 &= -\lambda^2 \dot{x}^n \frac{\partial}{\partial \tau} h_{mn} - \lambda \dot{x}^n \frac{\partial h_{m0}}{\partial x^n} + \lambda \dot{x}^n \frac{\partial h_{n0}}{\partial x^m} \\
 &= 2 \lambda^4 \dot{x}^m \frac{\partial}{\partial \tau} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) - 4 \lambda^4 \dot{x}^s \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} \eta^m + \frac{m_2}{r_2} \xi^m \right) \\
 &+ 4 \lambda^4 \dot{x}^s \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} \eta^s + \frac{m_2}{r_2} \xi^s \right) + 0 (\lambda^6), \tag{27}
 \end{aligned}$$

$$\begin{aligned}
 \lambda^2 \dot{x}^\rho \dot{x}^\sigma \Gamma_{\alpha\alpha}^m &= \lambda^2 \dot{x}^\rho \dot{x}^\sigma \frac{1}{2} g^{m\mu} \left[\frac{\partial h_{\rho\mu}}{\partial x^\sigma} + \frac{\partial h_{\rho\mu}}{\partial x^\sigma} - \frac{\partial h_{\rho\sigma}}{\partial x^\mu} \right] \\
 &= 2 \lambda^4 \dot{x}^m \dot{x}^\sigma \frac{\partial}{\partial x^\sigma} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) - \lambda^4 \dot{x}^\sigma \dot{x}^\sigma \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) + 0 (\lambda^6). \tag{28}
 \end{aligned}$$

$$\begin{aligned}
 &- \frac{1}{2} \lambda^2 \dot{x}^m \frac{d}{d\tau} \log [g_{00} + 2 g_{n0} \lambda \dot{x}^n + \lambda^2 \dot{x}^\rho \dot{x}^\sigma g_{\rho\sigma}] \\
 &= -\frac{1}{2} \lambda^2 \dot{x}^m \frac{d}{d\tau} \log (1 + h_{00} - \lambda^2 \dot{x}^\rho \dot{x}^\rho) + 0 (\lambda^6) \\
 &= -\frac{1}{2} \lambda^4 \dot{x}^m \frac{d}{d\tau} \left[-\frac{2m_1}{r_1} - \frac{2m_2}{r_2} - \dot{x}^\rho \dot{x}^\rho \right] + 0 (\lambda^6) \tag{29}
 \end{aligned}$$

Making the necessary substitutions for the various terms in (19) we get

$$\begin{aligned}
 &\lambda^2 \left[\dot{x}^m - \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \right] \\
 &= \lambda^4 \left\{ \frac{1}{2} \frac{\partial}{\partial x^m} \left(m_1 \frac{\partial^2 r_1}{\partial \tau^2} + m_2 \frac{\partial^2 r_2}{\partial \tau^2} \right) - 2 \dot{x}^m \frac{\partial}{\partial \tau} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) - \dot{x}^m \frac{d}{d\tau} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \right. \\
 &\quad \left. - \dot{x}^m \dot{x}^\rho \dot{x}^\sigma + \dot{x}^s \left[4 \eta^m \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} \right) + 4 \xi^m \frac{\partial}{\partial x^s} \left(\frac{m_2}{r_2} \right) - 2 \dot{x}^m \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
& + 4 \dot{\eta}^m \frac{\partial}{\partial \tau} \left(\frac{m_1}{r_1} \right) + \frac{4 m_1}{r_1} \eta^m + 4 \dot{\xi}^m \frac{\partial}{\partial \tau} \left(\frac{m_2}{r_2} \right) + 4 \frac{m_2}{r_2} \xi^m \\
& + \frac{\partial}{\partial x^m} \left[-2 \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right)^2 + \frac{m_1}{r_1} \left(\frac{2}{3} \eta^s \eta^s - \frac{m_2}{r_{12}} \right) + \frac{m_2}{r_2} \left(\frac{2}{3} \xi^s \xi^s - \frac{m_1}{r_{12}} \right) \right] \\
& - 4 x^s \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} \dot{\eta}^s + \frac{m_2}{r_2} \dot{\xi}^s \right) + x^s x^s \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \} + 0 (\lambda^6). \quad (30)
\end{aligned}$$

In simplifying (30) we note that

$$\frac{\partial r_1}{\partial \tau} = - \frac{\partial r_1}{\partial x^s} \eta^s \quad (31)$$

$$\frac{\partial^2 r_1}{\partial \tau^2} = - \frac{\partial r_1}{\partial x^s} \eta^s + \frac{\partial^2 r_1}{\partial x^p \partial x^q} \dot{\eta}^p \eta^q \quad (32)$$

$$\frac{\partial^2 r_2}{\partial \tau^2} = - \frac{\partial r_2}{\partial x^s} \xi^s + \frac{\partial^2 r_2}{\partial x^p \partial x^q} \xi^p \xi^q \quad (33)$$

$$\frac{\partial}{\partial \tau} \left(\frac{m_1}{r_1} \right) = \eta^s \frac{\partial}{\partial \eta^s} \left(\frac{m_1}{r_1} \right) = - \dot{\eta}^s \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} \right) \quad (34)$$

$$\frac{\partial}{\partial \tau} \left(\frac{m_2}{r_2} \right) = - \xi^s \frac{\partial}{\partial x^s} \left(\frac{m_2}{r_2} \right) \quad (35)$$

$$\frac{d}{d\tau} \left(\frac{m_1}{r_1} \right) = (x^s - \dot{\eta}^s) \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} \right) \quad (36)$$

$$\frac{d}{d\tau} \left(\frac{m_2}{r_2} \right) = (x^s - \xi^s) \frac{\partial}{\partial x^s} \left(\frac{m_2}{r_2} \right) \quad (37)$$

$$x^s = \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) + 0 (\lambda^2) \quad (38)$$

$$\eta^s = \frac{\partial}{\partial x^s} \left(\frac{m_2}{r_{12}} \right) + 0 (\lambda^2) \quad (39)$$

$$\xi^s = \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_{12}} \right) + 0 (\lambda^2). \quad (40)$$

So, on neglecting terms of the order of λ^6 we get from (30)

$$\begin{aligned}
& \lambda^2 \left[x^m - \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} + \frac{m_2}{r_2} \right) \right] \\
& = \lambda^6 \left\{ \left[x^s x^s - 4 x^s \dot{\eta}^s + \frac{2}{3} \eta^s \dot{\eta}^s - \frac{4 m_1}{r_1} - \frac{4 m_2}{r_2} - \frac{2 m_2}{r_{12}} \right] \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_1} \right) \right. \\
& + \left[x^s x^s - 4 x^s \xi^s + \frac{2}{3} \xi^s \dot{\xi}^s - \frac{4 m_1}{r_1} - \frac{4 m_2}{r_2} - \frac{2 m_1}{r_{12}} \right] \frac{\partial}{\partial x^m} \left(\frac{m_2}{r_2} \right) \\
& \left. + [4 x^s (\eta^m - \xi^m) + 3 x^m \dot{\eta}^s - 4 \dot{\eta}^m \eta^s] \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_1} \right) \right\}
\end{aligned}$$

$$\begin{aligned}
 & + [4 \dot{x}^s (\xi^m - x^m) + 3 \dot{x}^m \xi^s - 4 \xi^m \xi^s] \frac{\partial}{\partial x^s} \left(\frac{m_2}{r_2} \right) \\
 & + \frac{4 m_1}{r_1} \frac{\partial}{\partial x^m} \left(\frac{m_2}{r_{12}} \right) + \frac{4 m_2}{r_2} \frac{\partial}{\partial x^m} \left(\frac{m_1}{r_{12}} \right) - \frac{1}{2} m_1 \left(\frac{\partial r_1}{\partial x^s} \right) \frac{\partial}{\partial x^s} \left(\frac{m_2}{r_{12}} \right) \\
 & \quad - \frac{1}{2} m_2 \left(\frac{\partial r_2}{\partial x^s} \right) \frac{\partial}{\partial x^s} \left(\frac{m_1}{r_{12}} \right) \\
 & + \frac{1}{2} m_1 \frac{\partial^3 r_1}{\partial x^m \partial x^p \partial x^q} \dot{\eta}^p \dot{\eta}^q + \frac{1}{2} m_2 \frac{\partial^3 r_2}{\partial x^m \partial x^p \partial x^q} \xi^p \xi^q \} \quad (41)
 \end{aligned}$$

If by changing the density of the first body we can make approximately,

$$m_1 = 0, m_1/r_1 = 0, \partial/\partial x^m (m_1/r_1) = 0 \quad (42)$$

we have

$$r_1 = r_{12} \quad (43)$$

and (41) reduces to

$$\begin{aligned}
 x^m - \frac{\partial}{\partial x^m} \left(\frac{m_2}{r_{12}} \right) = \lambda^4 m_2 \left\{ \left[\dot{x}^s \dot{x}^s + \frac{3}{2} \xi^s \xi^s - 4 \dot{x}^s \xi^s - \frac{4 m_2}{r_2} \right] \frac{\partial}{\partial x^m} \left(\frac{1}{r_{12}} \right) \right. \\
 \left. + [4 \dot{x}^s (\xi^m - x^m) + 3 \dot{x}^m \xi^s - 4 \xi^m \xi^s] \frac{\partial}{\partial x^s} \left(\frac{1}{r_{12}} \right) \right. \\
 \left. + \frac{1}{2} \frac{\partial^3 r_{12}}{\partial x^m \partial x^p \partial x^q} \xi^p \xi^q \right\} \quad (44)
 \end{aligned}$$

This is precisely what (17) reduces to when $m_1 = 0$. Hence the consistency of the new method with the geodesic postulate is established as far as this test goes. We could have tested the consistency further by comparing (41) itself with the form of equations for m_1 in the field of m_1 and m_2 , as given by the new method, when m_2 is negligible. E I H does not give the three-body equations and we have therefore to be content with the comparison afforded by the two-body problem. As far as our calculations of the three-body problem go (41) is found to be consistent with the corresponding form of Einstein's equations of motion.

§ 4 We will now proceed to consider how it is possible to reconcile the equations of motion obtained from

$$G_{\mu\nu} = 0$$

with the geodesic postulate. The clue is provided by the identities,

$$(G^{\mu\nu} = \frac{1}{2} G g^{\mu\nu})_{,\nu} = 0. \quad (45)$$

Certain functions $\dot{\bar{C}}_m(\tau)$ which enter the method of E I H have the property that when all $\dot{\bar{C}}_m \rightarrow 0$, $G_{\mu\nu}$ also tends to zero. If $\dot{\bar{C}}_m \neq 0$ for one value of m or k , $G_{\mu\nu} \neq 0$ also. Now

$$\dot{\bar{C}}_m = 0 \quad m = 1, 2, 3 \quad (46)$$

are the equations of motion of the k th particle of the system in Einstein's method. Let us see how $G_{\mu\nu}$ can be made to tend to zero so that when the mass of the k th particle is zero (46) is consistent with the equations of geodesics. When $G_{\mu\nu} \neq 0$ its value can be expressed in the normal form

$$G_{\mu\nu} = \rho_0 u_\mu u_\nu - \rho_1 v_\mu v_\nu - \rho_2 w_\mu w_\nu - \rho_3 x_\mu x_\nu, \quad (47)$$

where u_μ is a timelike unit vector and v_μ , w_μ and x_μ are spacelike unit vectors. Also

$$G = \rho_0 + \rho_1 + \rho_2 + \rho_3 \quad (48)$$

$$\text{and} \quad g_{\mu\nu} = u_\mu u_\nu - (v_\mu v_\nu + w_\mu w_\nu + x_\mu x_\nu) \quad (49)$$

The identities (45) now become

$$\{(\rho_0 - \rho_1 - \rho_2 - \rho_3) u^\mu u^\nu + (\rho_0 - \rho_1 + \rho_2 + \rho_3) v^\mu v^\nu + (\rho_0 + \rho_1 - \rho_2 + \rho_3) w^\mu w^\nu + (\rho_0 + \rho_1 + \rho_2 - \rho_3) x^\mu x^\nu\}_\nu = 0 \quad (50)$$

$$G_{\mu\nu} \rightarrow 0 \quad \text{as } \rho_\mu \rightarrow 0 \quad (51)$$

Hence (50) will reduce to the equations of a geodesic,

$$(u^\nu)_\nu u^\nu = 0$$

when along with $\rho_\mu \rightarrow 0$ we have also

$$\frac{\{(\rho_0 - \rho_1 + \rho_2 + \rho_3) v^\mu v^\nu + (\rho_0 + \rho_1 - \rho_2 + \rho_3) w^\mu w^\nu + (\rho_0 + \rho_1 + \rho_2 - \rho_3) x^\mu x^\nu\}_\nu}{\{(\rho_0 - \rho_1 - \rho_2 - \rho_3) u^\mu\}_\nu} \rightarrow 0. \quad (52)$$

It is not necessary that the conditions (52) will always be satisfied. It is the special virtue of Einstein's method that (52) is satisfied at least upto 0 (λ^0). Herein lies an explanation of the consistency with the geodesic postulate as discovered by us. Incidentally it is of some astronomical interest to observe that if the bodies of masses m_1 and m_2 are looked upon as the earth and the sun the equation (41) obtained by us gives the motion of the moon in the field of the others.

Summary

We derive an equation (41) for the geodesics in the field of two bodies as given by Einstein, Infeld and Hoffmann. It is shown that when $m_1 = 0$ the equation reduces to that of the two-body problem (17) obtained without any reference to the geodesic postulate. This is the main result of the paper. Although Einstein's new method of deriving gravitational equations of motion is based on the field equations only we show how it can be consistent with the geodesic postulate if the field tensor tends to zero in a particular manner.

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THE EFFECT OF SUNSET ON ATMOSPHERICS

BY N S SUBBA RAO, M A

(*Annamalai University, Annamalai-nagar, S India*)

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Introduction

IN recent years the study of atmospherics has been made from several points of view. The credit for starting a systematic study goes to Appleton, Watson and Watt (1923), who during their early researches recorded the wave forms of atmospherics with a cathode-ray oscillograph and classified them into aperiodic, periodic and quasi-periodic types. It was also found that in many cases, the main structure of the atmospheric was supplemented by ripples of short duration.

Atmospherics and Lightning

A study of lightning and its relationship to atmospherics has been made in great detail by several observers. Besides studying the wave forms of atmospherics, Watt and Appleton have analysed some 15,000 directional bearings and located the regions from which atmospherics originate. They found that 94% of the atmospherics could directly be associated with contemporary rainfall areas, 35% located in front of cyclonic depressions and 15% with thunder and lightning. At about the same time, a detailed study of the sudden changes in the electric field accompanying a lightning flash was carried out by Appleton, Watt and Herd (1926). It was found that lightning discharges are capable of producing radiation fields similar in wave form and magnitudes to those of atmospherics of distant origin.

Schonland and Collens (1933), from a study of the photographs of 50 separate lightning discharges from two thunderstorms, with the Boys' rotating lens camera, found that many apparently continuous discharges are made up of a number of discrete strokes varying in number from 1 to 12 separated by short periods. The majority of the strokes were found to be double and to consist of a dart-like, downward-moving leader stroke, followed immediately on arrival at the ground by a more intense flame-like, upward-moving main stroke. It was further found that the duration of a complete lightning flash is often of the order of 1 second, although later observers give much longer periods. Malan and Collens (1935) showed that each of these

strokes is composite consisting of a leader portion and the main stroke. The leader to the first stroke consists of a series of streamers moving in a step by step manner (stepped leader).

Appleton, Watson, Watt and Herd (1926) and Cairns (1927) and others who studied atmospherics with the aid of cathode-ray oscillographs give times of the order of milliseconds for the duration of atmospherics, while observations made in Australia, using an ordinary tuned receiving set and recording the motion of the string of an Einthoven galvanometer on moving photographic paper, have given durations ranging in most cases from 2 to 5 seconds. Munro and Webster (1934) examined the wave form of atmospherics with an aperiodic receiver and a cathode-ray oscillograph with a time base of slower period (1 second) and found that an atmospheric really consists of a number of discrete pulses separated by clear intervals. The sizes and separations of the component pulses were found to vary in an irregular manner and thus to give rise to the rough noises produced in a broadcast receiver.

The observations of Appleton, Watt and Herd were evidently made with such rapid time bases that only one of the constituent pulses was observed on each occasion. With a tuned receiving set, and reading with a galvanometer with a relatively long period, the constituent parts of an atmospheric are merged together and the duration recorded is that of the whole succession of pulses, i.e., the duration as it would appear to a broadcast listener.

It was pointed out by the author (1935), as a result of preliminary investigations on atmospherics carried out with the aid of a receiver tuned to a wavelength of 400 metres and a galvanometer of period 1 second, that the records show certain thickenings (Fig. 1) along the trace of the galvanometer motion. The number of thickenings indicates the number of separate impulses received by the galvanometer in any given interval, and these could be arranged into groups taking into consideration the rate at which they succeed each other. From Fig. 1 which is an enlargement of a section of one of the records it can easily be seen that the total duration of each atmospheric appears to be about 1/2 second, and the photographs show that the atmospherics recorded have a number of components ranging from 4 to 12. Each of these constituent impulses may have a fine structure, which cannot be revealed except when examined with a cathode-ray oscillograph. The dots may be considered as indicating the gross structure of an atmospheric and may be directly traced to the constituent strokes of a lightning discharge.

Norinder (1936) from simultaneous observations of atmospherics with the aid of loud speakers of radio receiving sets and corresponding records

with cathode-ray oscillographs, found two characteristic forms of atmospherics in connection with thunderstorms (1) the 'clicks' singular, discharges of a comparatively short period (up to 100 milliseconds) caused apparently by very short discharges within adjacent parts of a thundercloud, and (2) the 'grinders' consisting of repeated swarms of field variations extended over long intervals of time (200 to 400 milliseconds and in some cases even from 3000 to 4000 milliseconds) and caused by distant lightning discharges. Appleton, Watt and Herd (1926) pointed out that the individual atmospheric wave forms were either of an aperiodic or quasi-periodic electric disturbance of duration 2-3 milliseconds. High frequency ripples on the main gross structure were also observed and the interferent effects of atmospherics were attributed to such high frequency components rather than to the effect of the relatively slow main disturbance.

Appleton and Chapman (1937), by studying atmospherics of known (thunderstorm) origin, with improved apparatus, have given a more satisfactory account of the high frequency components and a complete picture of the evolution of the atmospheric from the original disturbance and also a detailed description of the remarkable sequence of alterations of wave form with distance. The analysis of radiation fields of atmospherics showed that the most frequent type is one with a single component, but after this the number of components 2 or 3, 4 or 5, occur with decreasing frequency. The analysis of some thousands of records of the net field changes due to lightning, with the aid of a string electrometer and later with a cathode-ray oscillograph, also showed that the most frequent type of discharge is one that takes place in a single step, but that the next most frequent number of steps is either two or three, double or triple discharges being equally frequent. Further the records show tendency for the atmospheric to occur in groups corresponding to the time sequence of partial discharges of varying intensity.

It was also shown that with increasing distance the total duration of atmospherics appears to increase, the wave form becoming more regular and the high frequency ripples less prominent. At a distance of about 200 kilometers the wave form of the atmospheric disturbance is determined practically entirely by the radiation field of the discharge. At still greater distances a slow tail of about two rounded half cycles developed.

Atmospherics and Thunderstorms

In all the above investigations an attempt has been made to study the wave form, duration and its variations with distance of atmospherics and to correlate it with the detailed studies of lightning as the source of atmospherics. Lightning has its origin in the existence in the lower atmosphere of certain

special type of meteorological conditions There is no lack of evidence that we must look to thunderstorms upto very considerable distances as important sources of atmospheric A thunderstorm from the point of view of a meteorologist is defined as a procedure in the atmosphere which is connected with disruptive discharges that ought to be visible or audible or both For their development, such discharges require charge accumulations and field forces along the discharge region, of dimensions which we are not yet able to reproduce in the laboratory These accumulations of charges and the building up of strong fields are thus defined as a thunderstorm when lightning has occurred within the active regions of the atmosphere

Observations on atmospheric with a narrow sector directional recorder by Munro, Wark and Higgins (1936) point to two main types of sources, which they classify as regular and irregular The regular ones are tropical thunderstorm areas and the irregular ones of lower activity are chiefly 'frontal' thunderstorms, associated with cold fronts These authors consider atmospheric as valuable in weather forecasting

Several attempts made to correlate the occurrence of atmospheric with weather conditions, to locate storm and thunderstorm areas with the aid of atmospheric have yielded very valuable information A large amount of work has been done by R Bureau and others (1926) who have reached the conclusion that atmospheric are the phenomena that best give evidence of the passing of a meteorological disturbance in tropical regions The other meteorological variables only indicate that passing in a much less regular manner Moreover they only give evidence of the meteorological disturbance when it has reached the observing station while atmospheric announce it some hours in advance

It is now generally agreed that the majority of atmospheric encountered in radio communication originate in lightning flashes, and the prominent source of the world's supply at any hour lies in a land where it is summer afternoon (Watt, 1929) and India being one of the chief sources of atmospheric affords ample scope for study

A study of atmospheric especially of their relationship with meteorological conditions has been made by me for sometime past Prior to these investigations I had noticed that at certain times of the year atmospheric disturbances were more intense on short waves than on the medium waves, although, as a general rule, atmospheric activity is very much greater on the medium waves, and further that the periods of maximum activity on the short waves did not always coincide with similar periods on the medium waves It was therefore expected that a study of these differences might

give a clue to the identification of particular types of disturbances with definite types of meteorological conditions.

Experiment

General Plan of Experiment

It therefore became necessary to take simultaneous records of atmospherics on two wavelengths, one in the medium wave band and another in the short wave band. In order to determine the diurnal variation of atmospherics, the study had to be carried out throughout the day. Continuous recording and the use of high speed recorders like the cathode-ray oscillograph were entirely out of the question on account of the high cost involved. Moreover the cathode-ray oscillograph is useful for the study of fine structure of atmospherics over short intervals of time and not well suited for the observations required in the present investigation. It was, therefore, decided that the study should be carried out with the aid of cheap and simple apparatus. Two radio receivers, each tuned to one of the chosen wavelengths together with a moving coil galvanometer having a comparatively large period (about 2 seconds) were employed, and the motion of the two spots of light reflected from the mirrors of the galvanometers were recorded photographically on bromide paper wound round a rotating drum.

In the place of continuous recording for all the 24 hours in the day, it was decided that sample records should be taken for about two minutes at intervals of one hour throughout the day. The two minute records were, from previous observations made by the author (1935), found to be sufficiently representative of the atmospheric activity at that period. An automatic device, details of which are given later, was constructed and used for making these records. With its aid, the two wireless receivers, the two galvanometer lamps and the motor used for rotating the drum were switched on at intervals of one hour. Records were then taken for about 2 minutes and the entire apparatus was switched off. This procedure was repeated throughout the day. Bromide paper of size 10" \times 12" was employed, one half of it being used for the medium wave records and the other for the short wave records. A sample record is given in Fig 2. The records, as explained earlier (Subba Rao, 1935) give information regarding the gross structure of the atmospheric and it is possible with their aid to identify the types of atmospherics described as 'clicks' and 'grinders' and to count the number of constituent impulses that make up any of the recorded atmospherics. These details are clearly visible in the enlargement of a small portion of one of the records (Fig 1) taken during the preliminary work.

In the course of this work on atmospherics a striking feature was noticed Atmospheric activity showed sudden increase after sunset To determine the precise nature of the effect of sunset, the records taken over a fortnight from 14th to 28th of August 1940, were analysed in detail The present paper discusses the results of this analysis. This particular period was chosen because atmospheric activity is generally very much lower than in summer, and the variation in atmospheric activity may be more clearly observed and their relationships to meteorological conditions more definitely established

Apparatus

The apparatus used in this investigation consists of two Pye 803 5-valve superhets with the AVC circuits put out of action One of these was tuned to a wavelength of 375 metres and the other to 37.5 metres Care was taken to see that there was no wireless station operating on these wavelengths The outputs of these receivers were shunted on to two moving coil galvanometers having periods of about 2 seconds As the atmospheric activity on medium waves was always greater than that on the short waves, only a fraction, approximately, $1/6$ ($4/25$) of the output of the first receiver is connected to the galvanometer The galvanometers were sufficiently damped so that when the coils were displaced they returned to rest always before the completion of one oscillation This was found to be essential in order to prevent the free oscillations of the galvanometer from interfering with the records of atmospherics

The rotating drum was driven by an electric motor geared down to the requisite speed After trying various speeds it was found that a speed corresponding to a traverse of the spot of light of $4\frac{1}{2}$ " per minute was found to be quite adequate for the purpose

Estimates of the intensities of atmospherics were made from the records on a scale of 5 When the atmospherics come in groups following each other in quick succession it is not possible to estimate the strength of the individual components of the groups and in such cases the throw of the galvanometer has been taken as representing the intensity of the group The number of components in any group could easily be counted from the records as each individual component of the atmospheric produces a slight thickening of the curve at the instant when it arrives as can be seen from Fig 1

Automatic Switching

The automatic switching was carried out with the aid of an ordinary clock regulated to keep correct time, a small circular ebonite disc (1.5 cm in diameter and 4 mm thick) was attached to the minute hand spindle. A strip

of brass A is embedded on the circumference of this disc and this strip is electrically connected to the spindle and through it to the body of the clock. Pressing against this disc is another strip of brass B insulated from the body. By means of the spring C the pressure of the strip B on the disc is maintained constant.

The body of the clock and the insulated strip are connected to two binding screws, H and K, to the ends of which the electrical circuit shown in the diagram is connected. The circuit consists of 6 Leclanche cells in series with an electromagnet. When the strip comes in contact with A, the electric circuit is closed and the magnet is energised. The position of the disc on the spindle is adjusted so that A comes into contact with B when the minute hand is at 60. Thus this relay circuit is closed automatically at intervals of one hour. The period for which the circuit is closed depends on the width of the brass piece A. In the present arrangement it has been adjusted to a period of about 3 minutes. The attachment of this device does not in any manner interfere with the normal working of the clock.

The energised electromagnet is made to close the main switch S, shown in Fig 3. A lever about 25 cm long is pivoted at O from an upright pillar. S is a spring whose tension can be adjusted with the aid of a screw. I is a soft iron piece carried by the lever above the poles of the electromagnet. The distance of this piece from the poles of the electromagnet can be altered by means of a screw not shown in the figure. At the free end of this rod, horizontally and at right angles to it, is fixed an ebonite strip which carries at its ends a thick copper rod R bent into the form indicated. When the electromagnet is energised, the rod is pulled down and closes the mercury switch S₁, which consists of the two cups 1 cm deep scooped out of ebonite and three-fourths full of mercury. These two mercury cups were connected in series with the mains 220 volts A.C. 50 cycles. To prevent sparking a suitable condenser is connected across these terminals.

As the receivers used in the present experiment were mains operated, with indirectly heated valves an interval of about 1 minute was required for heating the valves and bringing the sets into operation. The galvanometer lamps and the motor for rotating the drum had to be switched on only after the lapse of this interval. This delay was brought about by the introduction of a bimetal strip of brass and iron over which nichrome wire 26 s.w.g. was wound, necessary insulation being provided with the aid of thin mica sheets.

With the aid of a rheostat in series with the nichrome wire, the current through it could be regulated. This circuit is connected in parallel with the wireless receivers and is closed by the switch S₁. While the valves are getting

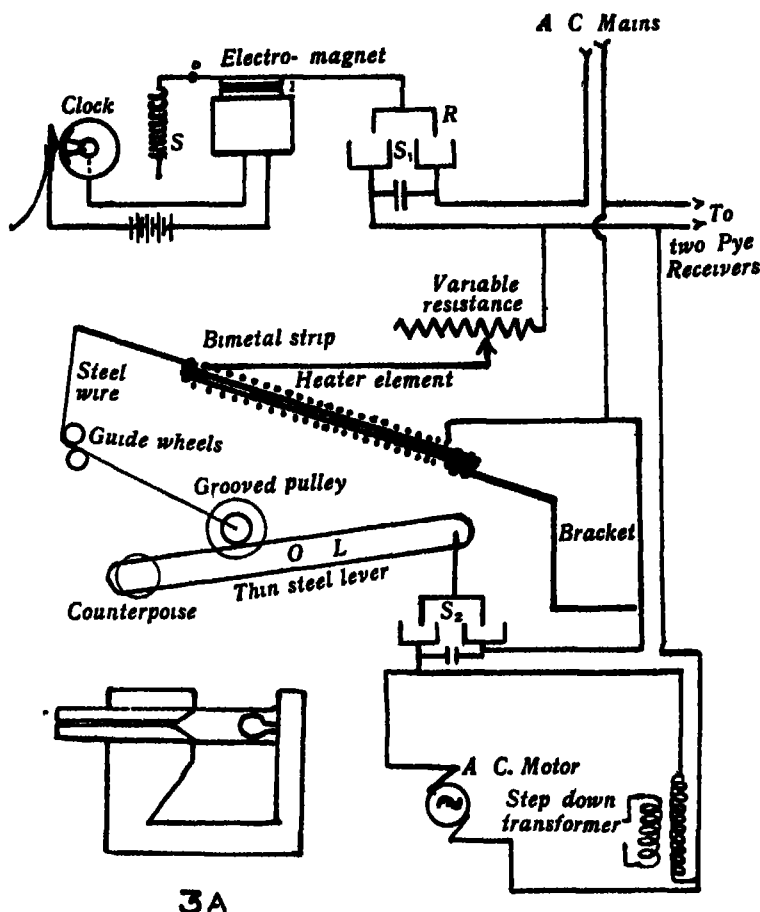


FIG 3

heated, the bimetal strip bends downwards and closes and the other main Switch S_2 through the lever L . The Switch S_2 closes the circuit of (1) the motor geared down to the required speed for rotating the drum and that of (2) the primary of a filament transformer (230 V to 4 V). Across the secondary of this transformer are connected two flash light lamps (3.5 V) with spherical bulbs and each of these is fitted at one end of a narrow tube of brass (15 cm long and 1 cm in diameter as shown in Fig 3A). To the other end of the tube is fitted a cap with a narrow circular slit. With the aid of this arrangement a narrow beam of light along the axis of the brass tubes is obtained and this in conjunction with the galvanometer mirror is employed for photographic registration. The image of the spot of light was finally sharply focussed on the drum with the aid of a convex lens ($f = 10$ cm).

Thus the recording apparatus was put into operation only about a minute after the receivers were switched on. The total duration for which the main switch S_1 is kept closed is 3 minutes and is controlled by the clock. The time for which the record is taken is equal to the difference between the duration for which S_1 is closed and the time taken by the bimetal strip to close S_2 . Thus keeping the total duration constant, the duration of the records can be altered at will with the aid of the rheostat.

In order to prevent arcing it was necessary to make the bimetal strip operate S_2 quickly. This was made possible by using a bimetal strip 10" long and attaching to its end a brass rod 4" long. This rod has to close S_2 at the end of one minute and to keep it closed for a period of about 2 minutes. During this two minutes interval, the heater current is still on and there is a progressive bending of the bimetal strip which means that sufficient clearance has to be provided for the bending of the strip even after the contact with the mercury cups of switch S_2 is made. This led to several mechanical difficulties which were finally solved by the design of the apparatus indicated in Fig. 3. A steel wire joined to the end of the brass rod after passing over two guide wheels was attached to a heavy brass grooved pulley running on a flat steel strip. This strip was pivoted at its centre and its equilibrium is suddenly upset, when the grooved pulley goes beyond a particular position. When this happens the switch S_2 is suddenly closed. Further bending of the metal strip only pushes the grooved pulley to the right but that does not introduce any mechanical difficulties. When S_1 is broken by the clock the current through the heater is switched off and the bimetal strip, the lever and the grooved pulley regain their original positions slowly and the above process is repeated every hour. The time taken by the bimetal strip to cool is about 8 minutes.

The Records

A sample record is given in Fig. 2. Only those atmospherics recorded on the medium waves from 9 hours on the 17th August 1940 to 13 hours on the 18th August 1940 are shown. This includes the period represented by curve 9a. The hours at which the records are taken are marked on the record. A look at the plate gives a rough idea of how atmospheric activity varies from hour to hour.

As pointed out in an earlier paper (Subba Rao, 1935) the kick of the galvanometer has been taken as a measure of the intensity of the atmospherics and the number of atmospherics (or atmospheric groups) reaching the observer in one minute could easily be counted. Although it was found convenient to plot the variations in the number of atmospherics received

per minute and in the intensity in the earlier investigation, a different procedure was adopted for the graphical representation of the results of the present investigation. The sum of all the impulses received by each one of the galvanometers during one minute has been taken as the measure of atmospheric activity and this quantity is shown on the Y-axis in the various graphs.

Records of the Atmospherics between the 14th and 28th August 1940

The ordinates indicate the times of the day at which the observations were made and the abscissæ the corresponding activity. The time corresponding to sunset is indicated by the thick dark line parallel to the Y-axis. The time of sunset varied from 18 hours 30 minutes on the 14th to 18 hours 22 minutes on the 28th. As it is not possible to indicate these slight variations on the graph, this line is drawn at 18 hours 24 minutes for the sake of convenience.

The thick line indicates activity on the medium waves and the thin line that on the short waves. The scales marked are common to both the graphs. It is however to be remembered that the curves do not represent relative activities on the medium and short waves as only a small portion ($1/6$) of the output of the receiver is coupled to the galvanometer in the first case and the entire amount in the other. Since the object of these preliminary investigations was to study how the activities on the two wavelengths respectively vary from hour to hour, the plots of the indications of the galvanometers were considered quite adequate for the purpose and no attempt has been made to reduce them to a common scale of measurement.

Results

As the activity of the medium waves forms the main subject of the study, the various records may be grouped as detailed below according to the effects observed on the medium waves before and after sunset.

Group 1.—Records in which atmospheric activity is practically nil before sunset, i.e., (at 18 hours) and rises very rapidly after sunset (at 19 hours).

Group 2.—Records with zero activity before sunset, with slight rise after sunset; showing increase by larger steps later.

Group 3.—Those showing activity even before sunset and slight increase of activity after sunset.

Group 4.—Those showing activity even before sunset but with a fall in activity after sunset.

Data relating to these records are abstracted in Table I

TABLE I

Group	Curve No	Date	Activity on medium wave at	
			18 hours	19 hours
I (Fig 4)	1a	20-8-40	5	80
	2a	21-8-40	0	69
	3a	23-8-40	0	51
II (Fig 5)	4a	18-8-40	4	19
	5a	19-8-40	0	12
	6a	22-8-40	0	15
	7a	24-8-40	0	13
III (Fig 6)	8a	14-8-40	10	13
	9a	17-8-40	25	45
IV (Fig 6)	10a	15-8-40	44	37
	11a	16-8-40	32	30

The first column indicates the group into which the particular record is placed. The second indicates the serial number of the curves in Figs 4, 5 and 6. The third column gives the date on which the effect of sunset is discussed. In the 4th and 5th columns are given the measures of total activity on the medium waves computed from the records of atmospherics as described earlier, at 18 hours and 19 hours. The sun sets at 18 hours 24 minutes.

The Characteristic Features of the Effect of Sunset on the Members of the Various Groups.

Group 1—This group consists of the records of atmospherics on the 20th, 21st and the 23rd August respectively. As indicated by the curves in Fig 4 the activity at 18 hours is zero, on the 21st and 23rd and practically zero (actually 5) on the 20th. It will be noticed that starting with practically zero activity before sunset, the activity rises to very large values, 80, 69 and 51 respectively on the three days at 19 hours.

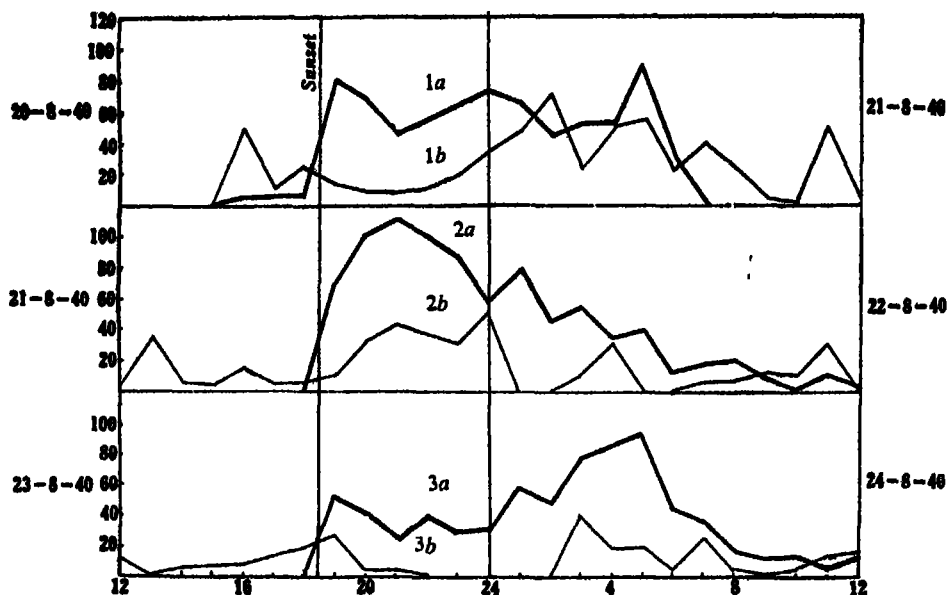


FIG 4

The Trigger Action

This sudden increase in activity within about half an hour after sunset reminds one of the *Trigger Action in the Atmosphere* described by Napier Shaw (1933). According to him two conditions have to be satisfied in order that a display of energy may occur automatically in the atmosphere. This display takes the form of a thunderstorm. The first condition to be satisfied is the existence of a state of liability in the atmosphere caused by the establishment of a thick layer in convective equilibrium. This is brought about by the heating effect of solar radiation on land. The other is the provision at the right moment of a sufficient quantity of air saturated with water vapour which is again brought about by the effect of solar radiation on water. The combination of these two is not more usual than a violent thunderstorm which is in many ways suggestive of trigger action.

When the thunderstorm commences atmospheric activity also commences and the measure of atmospheric activity will indicate the violence of the thunderstorm. From the data given in Table I, it is clear that the atmospheric or thunderstorm activity commences only after sunset and therefore it is very likely that it is the removal of solar radiation that operates the trigger. It is also reasonable to assume that there were in existence even before sunset conditions favourable for the starting of thunderstorm activity, the occurrence of lightning and the generation of atmospherics, but that the presence of

solar radiation was exercising a restraining influence thus preventing the starting of the thunderstorm. When the sun sets, this influence is removed and the thunderstorm activity commences and quickly attains large magnitudes even within the period of half an hour. On this view, therefore, the effect of sunset may aptly be described as trigger action.

Effect of Sunset

Although it is not possible to say exactly how solar radiation is responsible for the restraining influence, the studies of Schonland (1932) indicate that it is to the ionising influence of solar radiation that we must look for an explanation. Schonland has shown that a single lightning flash may easily discharge a cloud completely and that a fairly active cloud produces one flash every 20 seconds, which means that the cloud takes 20 seconds to recover its original state of electrification. He further finds that the recovery takes place so rapidly at the start, that if this rate continued, it would be able to restore the whole electrification in about 5 seconds. The recovery curve, however, is found to be exponential and this suggests that the initial rate may remain constant, but that, as the cloud charges grow, effects occur which tend to dissipate them and which are proportional to the quantity of charge present at any time. Thus at the moment just before a discharge most of the power of the machine is being expended in overcoming various leakage effects.

On the above view it is quite easy to explain the restraining influence of solar radiation on thunderstorm activity and the generation of atmospherics. Solar radiation tends to produce a state of ionisation in the atmosphere and this state greatly augments the leakage effects referred to above. Under the action of the greater leakage effects, it may happen that the field in the cloud never reaches the sparking value as long as the ionising influence of solar radiation is present. With the setting of the sun this influence is removed, the trigger is pulled and the electrostatic field builds up quickly and lightning flashes occur and the regular thunderstorm commences.

Group 2 —There are four records in Group 2. Here also the trigger action is quite evident although the activity at 7 (19 hours) is very much smaller than in records in Group 1. It can easily be seen from the curves (Fig. 5) that the activity reaches quite large values, not soon after sunset, but a few hours later.

Groups 3 and 4 —These consist of 2 curves each (Fig. 6). Activity before sunset is common to all these days but the sunset has affected them differently. On the 14th and 17th the trigger action of sunset is still evident although it is not so pronounced as in the records in the previous groups.

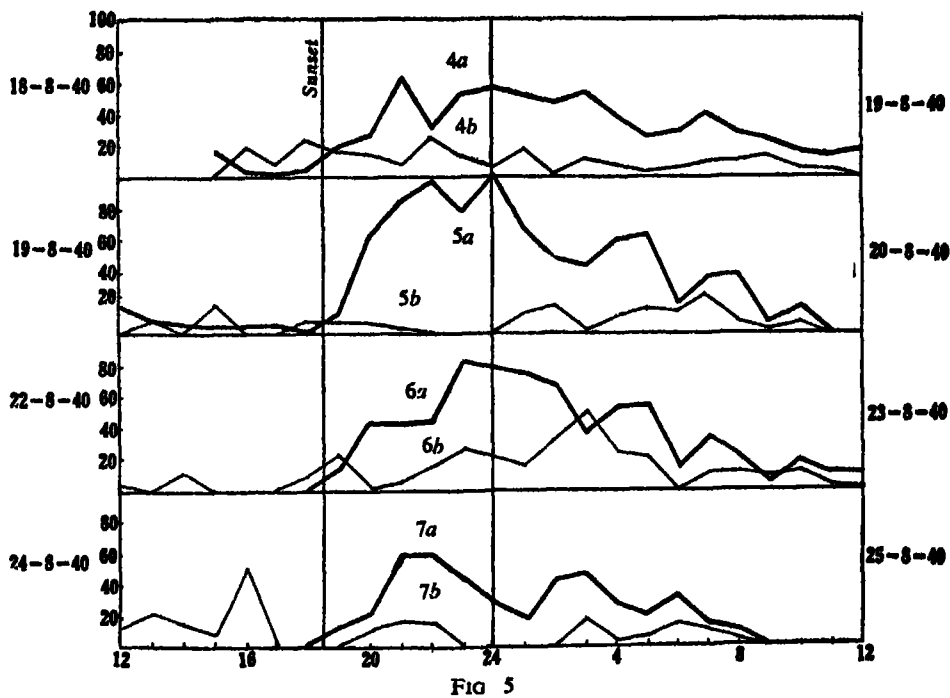


FIG 5

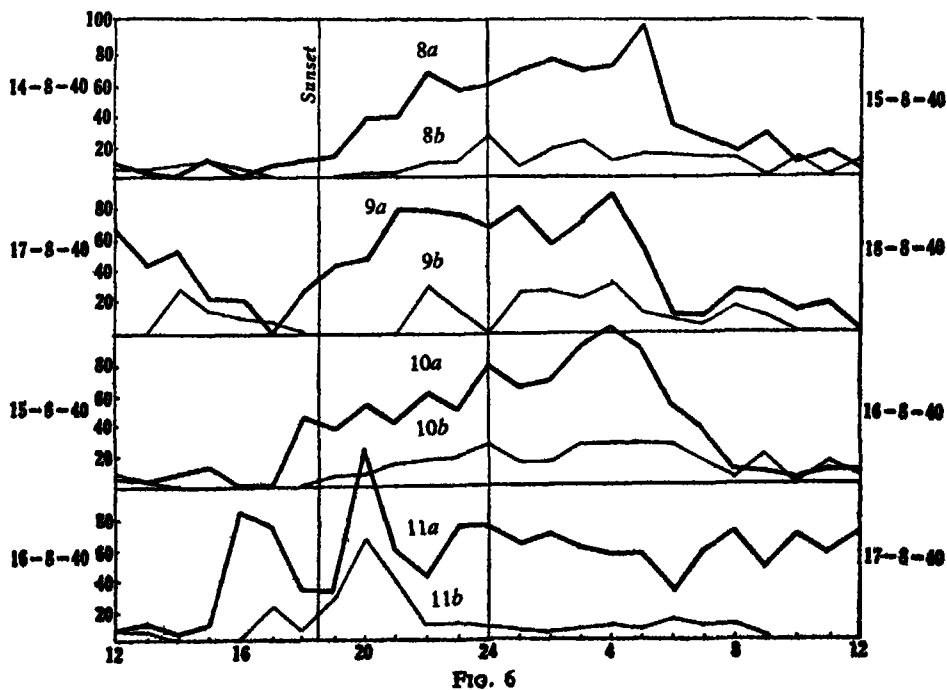


FIG. 6

On the 15th sunset brings about a reduction in activity, while on the 16th there is practically no change. These two records therefore do not seem to indicate the normal effect of sunset which brings about an increase in atmospheric activity.

Analysis of Atmospherics according to Intensity

This apparent discrepancy disappears when we consider the records from a different point of view. The activity on the various days at the specified times is due to a certain number of atmospherics. All of them naturally are not of the same intensity. If we examine the distribution of the number of atmospherics according to their intensities we obtain an insight into the actual mechanism of the effect of sunset on atmospherics. Such an analysis is given in Table II.

TABLE II
Classification of Atmospherics according to their Intensities

Group	Curve No	Date	Hour	No of atmospherics of intensities				No of Atm/min	Atmospheric activity
				2	3	4	5		
I	1a	20	18	1	1			2	5
			19	12	8	8		28	80
			20	7	9	7		23	69
	2a	21	18						
			19	12	11	3		26	69
			20	5	13	9	3	30	100
			21	4	9	8	9	30	112
	3a	23	18						
			19	15	3	3		21	51
			20	9	2	4		15	40
II	4a	18	18	2				2	4
			19	5	3			8	19
			20	5	3	2		10	27
	5a	19	21	9	4	7	1	21	63
			18						
			19	3	2			5	12
	6a	22	20	5	9	6		20	61
			21	4	11	9	1 (6)	25	83
			22	6	6	14	2	28	96
	7a	24	18						
			19	4	1	1		6	15
			20	2	8	4		14	44
			18						
			19	5	1			6	13
			20	5	4			9	22
			21	9	8	4		21	58
			22	7	11	3		21	59
III	8a	14	18	1	0	2		3	10
			19	5	1			6	13
			20	10	3	2		15	37
	9a	17	21	6	6	2		14	38
			18		3	4		7	25
			19	6	2	6		14	45
			20	7	1	7		15	45
			21	2	11	10		23	77

The first column gives the date of the record, the second, the hour at which the observations have been made. In the next four columns are indicated the number of atmospherics of intensities 2, 3, 4 and 5 respectively received during a total period of one minute. The next two columns indicate the total number of atmospherics received in one minute which is simply the total of the numbers in the previous four columns. The last column gives the total atmospheric activity which may be derived from the 3rd, 4th, 5th and 6th columns in the following way. Taking for example the observations on the 18th at 20 hours, there are 5 strokes of intensity 2, 3 of intensity 3 and 2 of intensity 4. The total number of atmospherics received per minute therefore is— $5 + 3 + 2 = 10$. The activity which has been defined earlier as the sum of the intensities of all the atmospherics received in a minute equals $(5 \times 2) + (3 \times 3) + (2 \times 4) = 27$. These numbers 10 and 27 are entered in columns 7 and 8 respectively.

General Characteristics

An examination of Table II brings out certain definite characteristics

1 *Trigger Action*—The effect of sunset is in all cases to bring about an increase in the number of atmospherics received per minute as well as in the total atmospheric activity. This is clearly indicative of the trigger action referred to earlier. The increase is observed to be very great on those days included in Group 1, less for those in Group 2 and very small for those in Group 3. In the cases included under Group 4 there is slight decrease, which means that the effect of sunset appears to bring about a decrease in atmospheric activity.

2 *The Progress of a Thunderstorm*—It will also be noticed that at the commencement of the storm initiated by sunset a number of atmospherics of low intensities (2 and 3) are observed. It is therefore quite reasonable to assume that lightning flashes are of small magnitudes and they are probably flashes which it is not easy to observe from the ground. In some cases atmospherics of low intensities are accompanied by atmospherics of larger intensities also; but generally the atmospherics of small intensities are more numerous than those of large intensities. With the progress of the thunderstorm there come into existence relatively more and more atmospherics of larger intensities, while those of smaller intensities become relatively few. This is very strikingly illustrated by the data included under Group 1. Curves 1, 2, 3 and 9 show that in these cases there are a considerable number of atmospherics of larger intensities even at 19 hours. The presence of atmospherics of large intensities even at 19 hours, about half an hour after sunset, is indicative of the existence of a special set of conditions in the atmosphere, and it seems to

be connected with the sudden rise in atmospheric activity between 18 and 19 hours which is characteristic of the members of this group. These special features are discussed in detail later. When the thunderstorm has commenced, its progress takes place in the manner described above. There is an increasingly greater number of atmospherics of large intensities with a corresponding diminution of those of smaller intensities.

This appears to be the normal method of development of a thunderstorm or atmospheric activity, *i.e.*, commencing with a large percentage of atmospherics of low intensities, the emphasis shifts to those of large intensities. In all the above-mentioned cases the initiation of the storm is by the setting of the sun. It will be interesting therefore to consider the progress of a thunderstorm which takes place during the day. Such an example is afforded by the activity on the 16th. There was severe thunderstorm activity between 15 and 18 hours on this day. The analysis of the number of atmospherics according to intensities between 15 and 24 hours is given in Table III.

TABLE III

Classification according to Intensities of Atmospherics between 15 and 22 Hours on the 16th August 1940

Section	Hour	No. of atmospherics of intensities				Total No	Total activity
		2	3	4	5 and above		
I	15	1	1	2		4	13
	16	5	20	3		28	82
	17		9	12		21	75
	18	1	6	3		10	32
II	19		6	3		9	30
	20		8	22	1, 1 (7)	32	124
	21	2	6	9		17	58
	22	4	7	3		14	41

The data may be divided into two sections. The first section refers to the period 15–18 hours. As indicated by curve 4 in Fig. 5 this corresponds to the evolution of the peak activity of 82 at 16 hours; at 16 hours the main body of atmospherics are of intensity 3, at 17 hours they are distributed among intensities 3 and 4 in the ratio of 9:12; at 18 hours, it is to be noted

that the main body of atmospherics has again shifted to lower intensities. By 18 hours the atmospheric activity has come down from 73 to 32.

The second section refers to the period 19-22 hours. This corresponds to the development of the peak activity of 124 at 20 hours. Here again it is noticed that nearly $\frac{2}{3}$ or 67% of the atmospherics are confined to intensity 3. While at 20 hours 70% are of intensity 4, at this time there have also developed atmospherics of intensities 5 and 7, and there are no atmospherics of intensity 2. At 21 hours there is a tendency for the development of atmospherics of lower intensities and once again we find as at 22 hours, that 30% of atmospherics are confined to intensity 2, 50% to intensity 3 and only 20% to intensity 4. By this time the atmospheric activity has come down in magnitude from 124 to 41.

In Table IV are given the contributions to the total activity obtained from atmospherics of various intensities. Next to each number the percentage contribution is indicated in brackets.

TABLE IV

Classification of Atmospherics between 15 and 22 Hours on the 16th August 1940, according to their Contribution to Total Activity

Hour	Atmospheric activity contributed to the total activity by atmospherics of intensities % contribution in brackets				Total activity
	2	3	4	5 and above	
15	2 (16)	3 (23)	8 (61)		13
16	10 (12)	60 (73)	12 (15)		82
17		27 (37)	48 (63)		75
18	2 (6)	18 (56)	12 (38)		32
19		18 (60)	12 (40)		30
20		24 (20)	88 (70)	12 (10)	124
21	4 (7)	18 (31)	36 (62)		58
22	8 (20)	21 (50)	12 (30)		41

This brings out more clearly the characteristics, not only of the process of building up of a thunderstorm as evidenced by the study of atmospherics but also the process of decay. The process of building up is accompanied by larger percentage contributions to the total atmospheric activity from atmospherics of higher intensities. The decay is evidenced by a decrease in this

percentage and a corresponding increase in the percentage contribution from atmospherics of lower intensities

It is also noticed from Table II that at certain periods there is practically no change in atmospheric activity or a slight decrease but that later the activity suddenly increases. Two such cases are discussed here as typical examples

The first example is taken from the 16th. As seen from Table IV, on the 16th between 18 and 19 hours there has practically been no change in activity (32 and 30) in spite of the fact that sunset occurred during this period. This seems to be contradictory to the invariable effect of sunset on atmospherics already described. But a little consideration shows that such is not the case. 16th is an exceptional day, thunderstorm activity reached a peak at 16 hours and from that time there has been a reduction in activity. At 18 hours activity is only 32. The first part of the Table shows that there is a tendency for atmospheric activity to decrease further but as actually observed there has been no change. We may therefore look upon sunset as being responsible for the preventing of a further decrease in atmospheric activity and also for providing the necessary conditions for bringing once more into being activity which attained a peak value at 20 hours.

The second example may be taken from the data for the 14th given in Table II. It is noticed that between 20 and 21 hours the atmospheric activity has remained unchanged, but the distribution of the number of atmospheric according to intensities is 10, 3, 2 at 20 hours, 6, 6, 2 at 21 hours clearly indicates that there is a tendency for atmospheric activity to increase. As can be seen from Fig 6, curve 11 *a*, there has been a gradual increase in activity through the night, the peak intensity being attained at 5 A M.

3 *Short Wave Activity Preceding Activity on the Medium Waves* — From an examination of curves 1, 2 and 3 (Fig 4) it will be noticed that there is considerable atmospheric activity on the short waves during the afternoons, this being the strongest on the 20th, less on the 21st and least on the 23rd. It is also interesting to note that the atmospheric activity at 19 hours on the three days in Group 1, is also in the same order 80 on the 20th, 69 on the 21st and 51 on the 23rd. These facts taken together seem to suggest that probably the two phenomena are interrelated, the short wave activity being an indication of the coming into existence of conditions preparatory to the onset of a thunderstorm. Unless such conditions are already present before sunset, the trigger action of sunset described above may not give rise to such pronounced atmospheric activity.

The conditions preparatory to the occurrence of lightning in a thundercloud are the building up of powerful electric fields and the storing up of large quantities of electricity. The electric field strength at which the spark which we call lightning takes place in air at ordinary pressure is 30,000 volts per centimetre. In a thundercloud the pressure is lower and the presence of small drops of water introduces a new and important factor.

The building up of these high potential is explained in different ways by Wilson and Simpson (1920 and 1927). According to Simpson the generation of electricity is due to the disruption of rain drops by an air current stronger than it could face without instability. On this hypothesis the orders of magnitude of the meteorological and electrical quantities involved are shown to be in accordance with the observations of Schonland and Craib (1927) in South Africa.

Macky (1933) as a result of investigations on the deformation and breaking up of water drops in strong electric fields, found that when exposed to increasing fields a drop of radius r becomes elongated until at a definite field strength, given in volts/cm by $F\sqrt{r} = 3875$, it becomes unstable and filaments are drawn out from the ends. When instability occurs a discharge passes through the drop in exactly the same manner as it would through a conductor pointed at both ends. The removal of water by the formation of filaments sets a limit to the size of the drops which can exist inside a thundercloud. Macky concludes that no drop larger than 0.15 cm in radius can exist in the fully charged cloud and that the critical value of the field at which a breakdown occurs is of the order of 10,000 volts/cm. The splitting up of the drops and the building up of the high potentials thus seem to be accompanied by the occurrence of small local sparks.

The mechanism suggested by Wilson as the cause of the opposite charges on large and small drops depends upon the presence in the cloud of a number of slow ions. In the earlier stages of development of a charged thundercloud these may arise from natural sources, but later on they will be supplied in numerous numbers by brush discharges from water drops drawn out by the field into pointed forms (Schonland, 1932).

Starting therefore with a cloud having large drops, the occurrence of these local sparks indicate that the charge and potentials are building up rapidly. As was pointed out by Larmor (1938), the lightning discharge in a thundercloud could be expected to begin at a place of maximum electric force (not potential) and to force its way through the atmosphere without tearing it, initially along the direction of the force.

Further according to Clark Maxwell, in an electrostatic field the force cannot be a maximum in free space. He therefore concludes that discharges must be initiated most probably within the thundercloud. Thus the spark and brush discharges referred to above might prepare the way for the occurrence of lightning flashes in very small regions of the thundercloud, flashes of such small magnitude, compared with those met with in a regular thunderstorm, that they cannot be observed from the ground either visually or with the aid of a camera.

These flashes however may give rise to atmospherics. Norinder (1936) is of opinion that some types of atmospherics specially those classified as "clicks" have their origin from field variations caused by such local sparks and brush discharges. It is very likely that these atmospherics have characteristics different from those ordinarily radiated from lightning during thunderstorms.

Simpson (1929) suggested that there can be little doubt that the resistance of a fully developed lightning channel when most highly ionised may well be less than the critical value and the channel therefore able to oscillate. These oscillations are superposed on the main current. The thundercloud itself has distributed capacity and inductance and it is reasonable to assume as Laby Nicholls, McNeil and Nickson (1940) have done that the electrical discharge which radiates an atmospheric is a damped oscillation with a period determined by the instantaneous resistance, inductance and capacity.

As pointed out by Lutkin (1939) the resistance increases as the channel ionisation decreases, while capacity to earth and also inductance increase as the length of the channel increases. In the case of the local discharges referred to above, we might suppose that in view of the smallness of the capacity and inductance involved that the atmospherics which arise from these discharges are likely to be more prominent on the short waves. From curves 1, 2 and 3 (Fig. 4) it is seen that in the afternoon of the 20th, 21st and 23rd there is considerable activity on the short waves, with nothing at all in the medium waves. Taking along with this the fact that the trigger action of sunset is most pronounced on these days, the short wave activity may be considered as indicative of the building up of the conditions in the atmosphere necessary for the onset of a powerful thunderstorm. The onset is however prevented as explained earlier by the ionising influence of the sun, so that when the sun sets the storm bursts with all its violence.

If this view be correct, we must expect the setting of the sun to bring about a type of distribution of the number of atmospherics according to intensity on the 20th, 21st and the 23rd which is different from that observed.

previously. The data abstracted here for convenience will illustrate this difference

TABLE V

Classification of Atmospheric on the 20th, 21st and 23rd August 1940 according to Intensity

Date	Hour	No of atmospheric of intensities				No of Atm /min	Atmospheric activity
		2	3	4	5		
20	18	1	1			2	5
	19	12	8	8		28	80
	20	7	9	7		23	69
21	18						
	19	12	11	3		26	69
	20	5	13	9	3	30	101
	21	4	9	8	9	30	112
23	18						
	19	15	3	3		21	51
	20	9	2	4		15	40

On the 20th just after sunset there are not only 12 atmospheric of intensity 2 but also 8 of intensity 3 and 8 of intensity 4. This is very unusual but later on with the progress of the storm the percentage of atmospheric of larger intensities increases with a corresponding diminution of those of smaller intensities.

The presence of a large number of atmospheric of large intensities is suggestive of the existence of a previous state of preparation and according to the explanation given above, this is clearly indicated by the short wave activity before sunset on these days

The presence of the large number of atmospheric of intensity 2 (12 on the 20th and 21st, and 15 on the 23rd indicate that atmospheric activity is not confined to the particular centre which has already been prepared, but that there are other centres brought into action by the effect of sunset. The experimental results obtained by Schonland (1938) show that successive multiple lightning strokes may arise as a result of the existence of separate generating centres at different places within the cloud and that we can assume

that these larger thunder clouds may be expected to possess several such generating centres. When once such activity has been initiated, we find that as long as the activity is increasing there are a larger percentage of atmospheric of greater intensities as pointed out earlier.

It is quite clear from the above that on certain days atmospheric activity reaches very high magnitudes even after a short duration of half an hour from sunset. This building up of atmospheric activity to high magnitudes in such short periods leads to the conclusion that the setting of the sun acts like a trigger. Atmospheric are due to lightning flashes accompanying thunderstorms. Even when the meteorological conditions are favourable for the occurrence of a thunderstorm, still the storm itself does not usually commence until after sunset. The solar radiation by augmenting the leakage effects inside a thundercloud, prevents the attainment of the necessary critical potentials for the passage of the lightning flash. When sunset occurs, this restraining influence is removed and the thunderstorm bursts with all its violence. The evidence for the existence of these conditions appears to be indicated by the appearance of atmospheric on the short waves a few hours before sunset. The study of the activity on short waves therefore seems to provide information regarding the preparation of the atmosphere for the onset of a powerful thunderstorm a few hours before its actual occurrence and thus gives advance information about the meteorological condition of the atmosphere.

At the commencement of atmospheric activity it is usual to find a large percentage of atmospheric of low intensities and sometimes practically none of higher intensities. But in some cases a large number of atmospheric of higher intensities appear along with those of lower intensities. These seem to indicate that necessary conditions have already been built up and that atmospheric activity has been prevented from occurring by the action of solar radiation. Sunset therefore brings about atmospheric with large intensities. As these occurred only on those days when atmospheric activity on the short waves was noticed during the previous afternoons, this lends additional support to the view that the study of activity on the short waves will be able to provide useful advance information regarding the meteorological condition of the atmosphere.

Thus it is evident that the study of atmospheric activity on the short waves simultaneously with those on medium waves will give results which would supplement each other and provide the necessary basis for correlating the nature of the observed atmospheric with meteorological conditions, which is the main purpose of the present investigation. The data collected during the half year July to December 1940 are being examined and the results will be published later.

A study of the curves reveals further that on those days on which the trigger action of sunset is most pronounced, the peak activity is reached very early in the night (about 8 P M), whereas on those days on which the trigger action of sunset is not so pronounced, the rate of growth of thunderstorm activity is slow and the peak activity is attained very much later in the night (between 10 P M and midnight)

Atmospherics and Meteorological Depressions

Before concluding, a few observations may be recorded which, though they have no direct relation to the subject of the present paper, are likely to be of some importance to the main object of the investigation. It will be seen from the curves given in Figs 4, 5 and 6 that atmospheric activity has been most intense at particular times on particular days. Observations made by the "Challenger" showed that the frequency of thunderstorms at sea had a pronounced maximum between 2 P M and 4 A M, while the occurrence of lightning only showed a maximum between 8 p m and 10 P M. Over land, heat thunderstorms occur during the afternoons but certain types of thunderstorms associated with the line of separation between warm and cold current show no preference to any hour of day or night.

Maxima of atmospheric activity on the medium waves are attained in the early morning on the following dates 15, 16, 18, 21 and 24. On most of these days, however, there has been practically no activity on the short waves. But from the afternoon of the 20th till the morning of the 22nd there has been almost continuous short wave activity. Whether this prolonged activity on the short waves is indicative of "the unsettled condition off the Circars' coast", reported in the *Indian Daily Weather Report* dated 19th August 1940, and whether the occurrence of a peak activity on the medium waves in the early hours of the morning of the 21st along with severe short wave activity is indicative of the fact that "the unsettled conditions off the Orissa Coast developed into a depression", as reported in the *Indian Daily Weather Report* of the 21st August 1940, is a matter which requires to be studied in detail. Further data are being collected and results will be published in due course.

Summary

The paper describes the results of observations on the nature of the Effect of Sunset on Atmospherics. An automatic device specially constructed for the purpose was employed and with its aid, records of atmospherics on two wavelengths (37.5 metres and 375 metres) were taken for about two minutes at intervals of one hour throughout the day.

The study has brought to light certain interesting features characteristic of the period of investigation, which extended for a fortnight in the month of

August 1940 and showed active monsoon conditions, particularly between the 11th and the 26th, in the Peninsula, the central parts of the country and North West India (*India Weather Review*, August 1940)

It is pointed out that (1) the effect of sunset on atmospherics is that of Trigger action, (2) the study of atmospherics can give advance information regarding the preparation of the atmosphere for the onset of a powerful thunderstorm and (3) prolonged atmospheric activity on the short waves appears to be connected with the formation of meteorological depressions

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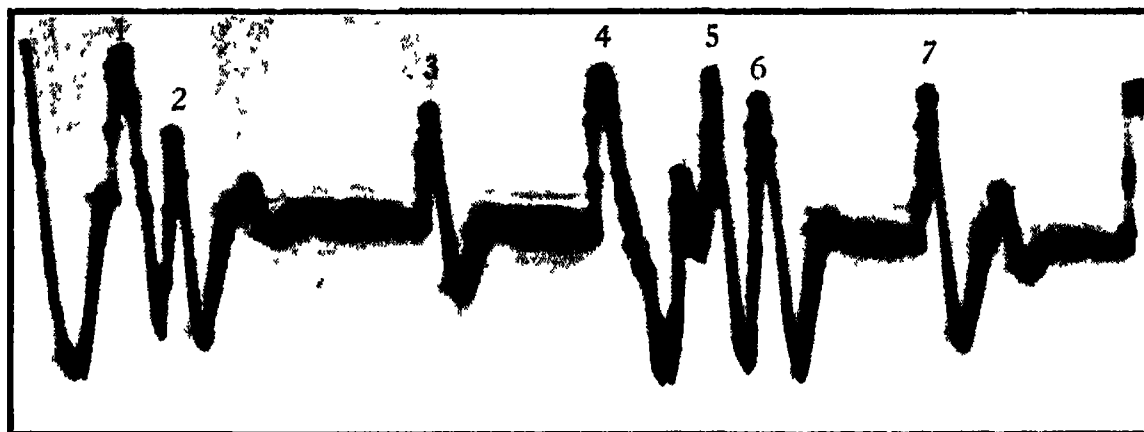


FIG. 1

Enlargement of a section of the record of atmospheres taken at 11 p.m. on 8-10 1954

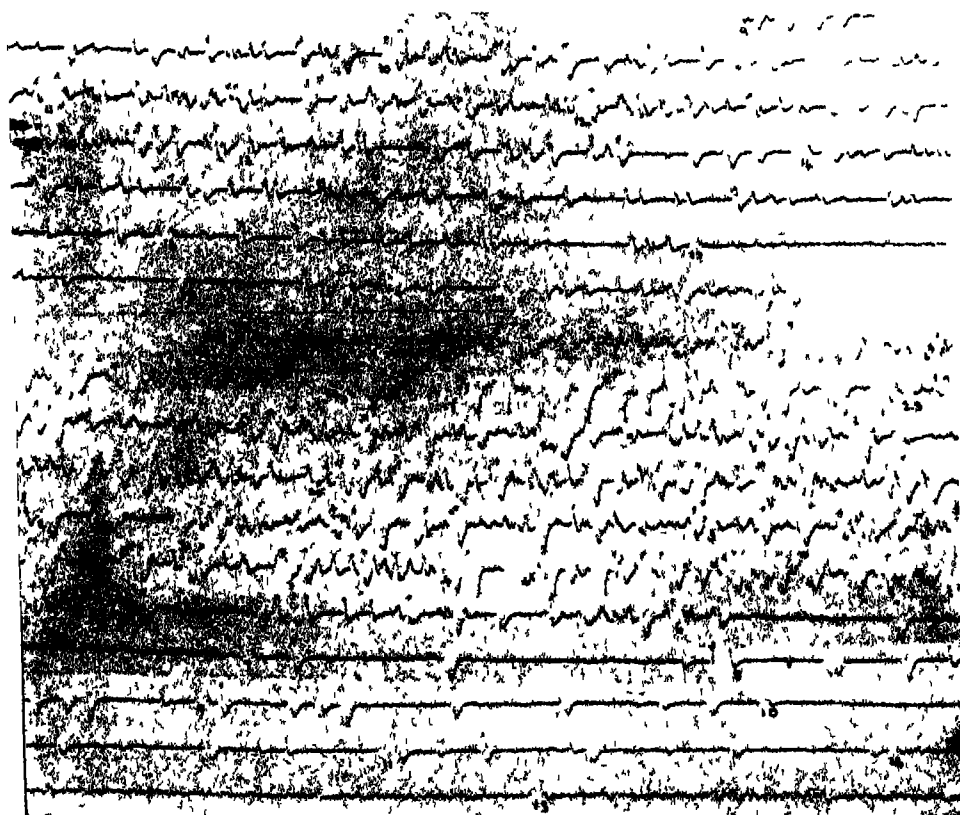


FIG. 2

Record of atmospheres from 9 hours on 17-8-1940 to 13 hours on 18.8.1940

CONICAL REFRACTION IN NAPHTHALENE CRYSTALS*

BY SIR C V RAMAN, V S RAJAGOPALAN
AND

T M K NEDUNGADI

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE phenomena of internal and external conical refraction in biaxial crystals predicted by Sir William Hamilton and observed by Humphrey Lloyd are amongst the most beautiful and striking effects arising in crystal optics. Following Lloyd's original experiments these phenomena are usually exhibited with aragonite, a polished plate of this crystal suitably mounted between apertures and a viewing lens being employed for the purpose. The angles of internal and external conical refraction in aragonite are however small, ($\chi = 1^\circ 52'$ and $\psi = 1^\circ 42'$ respectively), and the use of other crystals, e.g., tartaric acid with $\chi = 3^\circ 54'$ and $\psi = 3^\circ 58'$, and of sulphur for which $\chi = 7^\circ 11'$ and $\psi = 7^\circ 33'$ has therefore been sometimes suggested. It may be pointed out, however, that organic crystals of the aromatic class are specially suitable for the purpose. Naphthalene, in particular, exhibits birefringence in an exceptional degree, having as its principal indices 1.525, 1.722 and 1.945 respectively for $\lambda = 5461 \text{ \AA}$ and its conical angles ($\chi = 13^\circ 44'$ and $\psi = 13^\circ 51'$) are enormously larger than in aragonite. Large single crystals of naphthalene can easily be prepared (Hilmi-Benel, 1940, Nedungadi, 1941), and the substance is thus well suited for exhibiting the optical characters of biaxial crystals and especially conical refraction in a striking way.

It may be remarked that apart from the purely geometrical aspects of optical theory illustrated by the Hamilton-Lloyd experiments, certain physical aspects of the propagation of light in biaxial crystals arising in conical refraction are of great interest. One of these is the enormous concentration of energy which occurs along the axis of single-ray velocity within the crystal and along the axis of the cone of external refraction outside it (Raman, 1921, Raman and Tamma, 1922). The converse phenomenon associated with internal conical refraction has long been known and is referred to in

* A preliminary note on this subject appeared in *Nature* of the 1st March 1941

the literature as the Poggendorff dark circle. This was explained by Voigt (1905) as due to the attenuation of the energy of the incident pencil which occurs in single-wave propagation within the crystal. Both of these phenomena are well shown by naphthalene and in such manner as to bring out clearly their theoretical significance.

Conical refraction is often studied by viewing an illuminated pin-hole in focus through the crystal plate with a microscope or magnifying lens. It is generally supposed that what is then seen is internal conical refraction. That this is not quite correct was long ago pointed out (Raman, *loc cit*), but the matter was not then adequately discussed. Since the illuminated pin-hole is usually held close to the crystal and is backed by an extended source of light, the beam of light entering it is not restricted to any particular direction, and the effect observed is not therefore ascribable to internal conical refraction. Neither would it be altogether correct to ascribe it to external conical refraction, for, though with the pin-hole close to the crystal, a cone of light is incident on its first surface, no aperture limits the exit of the light from the second surface as in the Lloyd experiment. The focussed image of an illuminated pin-hole as seen in the microscope through the plate of crystal is formed by the entire bundle of rays issuing from the pin-hole and passing through the crystal and is thus a phenomenon distinct from either internal or external conical refraction, though related to both. As will be shown in this paper, the form of this image is determined by the curvature properties of the wave-surface in the crystal in the vicinity of the conical points. It is specially worthy of remark that when the microscope is focussed on the second surface of the crystal and not on the illuminated pin-hole, we see in the field of view an illuminated picture of the two sheets of the wave-surface, the conical point where they meet appearing as an intensely luminous centre, and the circle of contact with the tangent plane appearing as a dark ring (Fig 7 in Plate X).

2 Preparation of the Specimen

A clear block of naphthalene can be grown by slow crystallization from a melt. Pure naphthalene redistilled several times is collected in a pyrex glass tube of about half-an-inch diameter, with its lower end drawn out tapering to a sharp point. The tube is suspended in a vertical furnace kept at a temperature from 10° to 15° C above the melting point of naphthalene and gradually lowered out of it automatically by clock-work mechanism. Crystallisation starts at the tapering end of the tube and develops upwards. By proper control of the temperature of the furnace and of the rate of lowering of the tube, it is possible to get clear flawless blocks

of the single crystal of any desired length. It is removed from the container by momentarily heating the walls of the glass tube to a high temperature; the portion of the crystal in contact with it then melts and the crystal slips out.

As the crystal blocks prepared in this way do not possess any natural faces, advantage is taken of the fact that the axes of the optical and magnetic ellipsoids of the crystal roughly coincide to determine their orientation. The three magnetic axes of the crystal block may be determined by marking its preferred orientations in a strong magnetic field with different modes of suspension. The crystal block may be then cut with faces making any desired angle with these axes. To exhibit conical refraction, the naphthalene block should have its faces approximately normal to one of the primary optic axes, these being inclined at 42° to the acute bisectrix of the angle between them. For mounting the cut crystal, a flat surface is first ground and then quickly pressed on to a microscope cover slip kept at a temperature of about 40° above the melting point of naphthalene. The crystal face melts and wets the glass plate and immediately cools, thus resolidifying the melted layer as part of the single crystal in addition to making good optical contact with the glass. The second face of the plate is then treated in the same way. An alternative method of mounting is to grind the surfaces of the block smooth on a ground glass plate and then to polish them by rubbing quickly on a soft cloth stretched over a glass plate and moistened with a drop or two of xylene. Thin microscope cover clips may then be stuck on the faces with canada balsam. The mounted crystal may be conveniently fixed on a disc of aluminium having a central opening.

3. Method of Observation and Results

The angles of conical refraction in naphthalene are so large that with a fairly thick piece, the phenomena can be seen directly with the simplest possible arrangements. For a critical study of the effects, however, and especially for securing satisfactory photographs, it is convenient to use a microscope with a revolving and centering stage and a Federov universal stage attachment on which the crystal plate is placed so that it can be tilted and set with its optic axis accurately parallel to the axis of the microscope. A low-power objective and a high-power ocular should be employed so that, for the same effective magnification, the largest working distance between the upper surface of the crystal and the objective of the microscope can be secured. For observing conical refraction under the microscope, a relatively thin plate of naphthalene (say two to three millimetres thick) is quite suitable. It is easy with these arrangements to photograph the cone

of external conical refraction and the cylinder of internal conical refraction outside the crystal in the manner of the Hamilton-Lloyd experiments. It is also possible to examine the relationships between these effects and the nature of the optical images obtained when a point-source of light is viewed through the crystal either in or out of focus.

Figs 1-4 in Plate IX and Figs 5-8 in Plate X reproduce a series of photographs obtained with the microscope camera attachment to illustrate the phenomena of conical refraction in naphthalene, the monochromatic green light λ 5461 Å of the mercury arc being employed to avoid all disturbances due to chromatic aberration or dispersion. Fig 1 shows the hollow cone of external conical refraction as seen above the crystal, to photograph this, both the upper and lower surfaces of the crystal are covered up except for small apertures situated at the ends of the axis of single-ray velocity, the lower aperture being illuminated by a convergent pencil of light. Fig 2 shows the cylinder of internal conical refraction seen outside the crystal when a parallel beam of light is incident in the direction of the optic axis on the lower face of the crystal, to observe this, the lower face is covered by a screen with a small aperture and the second face is left uncovered. Figs 3 and 4 in Plate IX and Figs 5, 6, 7 and 8 in Plate X reproduce a consecutive series of photographs of a point source of light held close to the first surface and viewed through the crystal, Fig 3 is the image seen in focus, while the other photographs in the series are ultra-focal images obtained when the microscope objective is gradually drawn away from the crystal. As already mentioned in the Introduction, Fig 7 is the ultra-focal image of the point source of light obtained when the microscope is focussed on the second surface of the crystal. Fig 8 is the ultra-focal image obtained when the microscope is still further drawn up. In obtaining this series of six pictures, the source of light was an extremely fine hole (1μ in diameter) in an aluminium foil covering the lower surface on the crystal and illuminated by a convergent beam of light, while the second face of the crystal was left uncovered. The extreme sharpness of the circular ring seen in Fig 3 is particularly significant. *It is noteworthy also that the so-called Poggendorff dark circle does not appear in the focal image of the point source and develops only in the ultra-focal images.* The extremely bright point seen at the centre in Fig 7 (as also in Fig 8 and very feebly in Fig 2) is a noteworthy feature. This bright point in the ultra-focal image coincides with the end of the axis of single-ray velocity meeting the second surface of the crystal. This is shown by the fact that the second aperture for observing the cone of external conical refraction above the crystal (Fig 1) has to be placed exactly at the same point so as to admit the light passing through the crystal. It is

evident from the series of pictures *that the axis of single-ray velocity and the conical point on the wave-surface are loci of intense concentration of energy within the crystal, while the circle of contact where the wave-surface touches the tangent plane is a locus of vanishingly small energy*

4 *Image Formation with a Biaxial Crystal*

It is well known (Stokes, 1877 and Walker, 1904) that the image of a point source of light seen through a crystalline plate exhibits astigmatism, being drawn out into a line perpendicular to the plane of principal curvature. For a biaxial crystal there are, in general, no fewer than four distinct positions of best focus determined by the orientation of the plate and by the principal radii of curvature of each of the two sheets of the wave-surface. In our present problem, we are concerned with the curvature of the wave-surface in the vicinity of the conical point and especially along the circle of contact with the tangent plane. At the conical point, one of the principal radii of curvature for each of the two sheets of the wave-surface vanishes, while the other two radii are

$$\rho_1 = b \text{ and } \rho_2 = (a^2 + c^2 - b^2)^{3/2}/ac$$

At points along the circle of contact, one of the principal radii of curvature of each of the two sheets becomes infinite, while the other radius of curvature is

$$\rho = b(a^2 - r^2)(c^2 - r^2) / (a^2 - b^2)(c^2 - b^2),$$

r being the length of the line joining the origin with any specified point on the circle of contact. At the two points where this circle cuts the circular and elliptic sections of the wave-surface respectively, the radii of curvature are

$$\rho_1' = b \text{ and } \rho_2' = b^3/a^2c^2$$

In the case of naphthalene, b^2 and ac are practically identical, as is readily seen from the numerical values of the principal refractive indices. As a consequence of this, also, the angles of internal and external conical refraction are practically identical. Hence, while one of the principal radii of curvature of the wave-surface is infinite along the circle of contact, the other radius of curvature is practically constant and equal to b at all points on the circle and changes only slowly as we move away from the circle along the wave-surface either towards or away from the conical point. Accordingly, the astigmatism of the rays emerging from the plate results in an exceptionally simple form of the image, namely a sharply focussed circular ring having the same diameter as the circle in which the wave-surface makes contact with the second surface of the crystal.

necessarily alters continually. The rays reaching the upper surface of crystal within the circle of contact bend inwards, while those outside the circle bend outwards, a gap appearing between them owing to the vanishing of the rays at points along the circle. The rays that bend inwards appear to converge rapidly in intensity as they approach the centre of the field; the centre appears as a luminous point from which the rays appear to diverge, and the focal plane of the microscope coincides with the upper surface of the crystal.

The radiations from the point source entering the crystal may be regarded as an assembly of plane waves with coherent phase-relationships crossing at that point. Entering the crystal, their directions of travel are altered, and the resultant distribution of the energy stream within the crystal is determined by their superposition. Along the axis of single-ray refraction, the lines of energy flow of numerous sets of plane waves coincide, and the density of the energy flow is therefore a maximum on this line. On the other hand, along the so-called cone of inner conical refraction, the energy flow of a single set of plane-waves is divided up and the energy is therefore a minimum. Since the disturbance emerging from the crystal is determined by the superposition of the plane waves refracted outwards, the energy flow outside would be closely related to the special character of the energy flow within the crystal. Actually, the bright spot at the centre of the field may be traced for a great distance outside the crystal. The bright spot is, in effect, a spectral image of the original point source, its position varying with the wave-length of the light used (Raman and Gammal, *loc. cit.*).

5. Summary

The angles of internal and external conical refraction for naphthalene are exceptionally large (both about $13^{\circ} 45'$), and the substance is therefore exceptionally well suited for exhibiting these phenomena as well as for a study of the same. A series of eight photographs is reproduced with description and is discussed in detail. The following noteworthy effects are observed by the crystal. The so-called Poggendorff dark circle appears only in internal conical refraction and is an ultra-focal phenomenon, disappearing when the image of a point source of light seen in exact focus through the crystal plate, the image being then a single circular ring which is extremely bright. In external conical refraction we have an effect converse to the Poggendorff phenomenon, *viz.*, a concentration of energy at the conical surface of the wave-surface and therefore also along the axis of single-ray refraction. When the microscope is focussed on the second surface of the

FIG. 1



FIG. 2

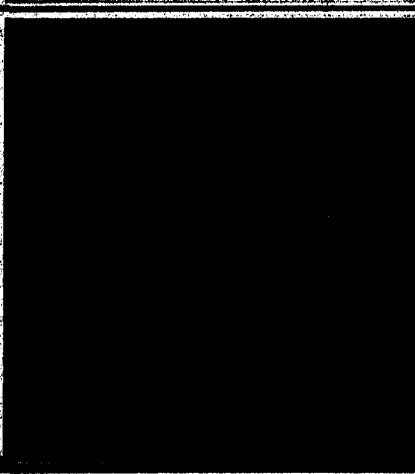


FIG. 3

FIG. 4

Illustrating Conical Refraction in a Naphthalene Crystal

FIG. 5

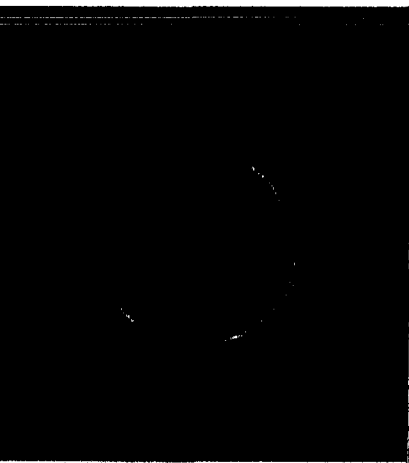


FIG. 6

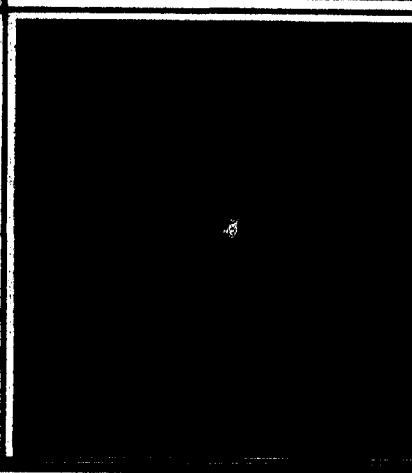
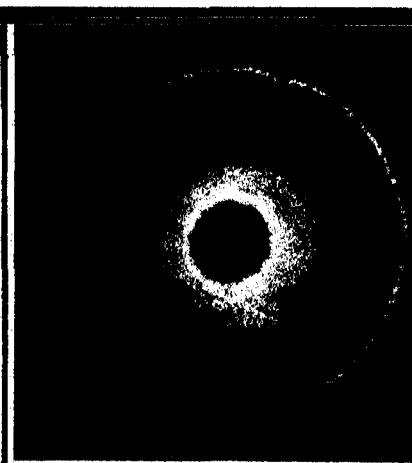


FIG. 7

FIG. 8

Illustrating Conical Refraction in a Naphthalene Crystal

crystal and not on the source of light, the field of view exhibits a picture of the wave-surface in two sheets, their intersection appearing as an intensely luminous point and the tangent plane to the surface as a dark ring

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NEW METHODS IN THE STUDY OF LIGHT SCATTERING*

Part I. Basic Ideas

BY SIR C V RAMAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE scattering of light in material media may be considered from two distinct points of view. The first is that of the colloid chemist or biologist, the opalescence or Tyndall effect exhibited by whose media is related to the number, size and structure of the particles dispersed in them. The other point of view is that of the spectroscopist investigating the scattering of light in transparent substances and its relation to the molecular structure and the state of molecular aggregation. There is obviously a wide difference in the aims and methods of study adopted by these two groups of workers. This should not be permitted, however to obscure the essential similarities in the phenomena with which they are concerned. We have only one to mention some specific examples, viz., optical glass, phenol-water mixtures, protein solutions and rubber dissolved in organic solvents, to realise the futility of setting out any rigid line of demarcation between "colloid" or turbid media, and "molecular" or transparent ones. Any such distinction must be conventional rather than logical. It will be realised, therefore, that the exchange of ideas and methods between the two fields of research should be of great importance for the progress of both.

2 The Reciprocity Relation

An important step in the unification of colloid and molecular optics was taken by Dr R S Krishnan (1934-1939) in his investigations at this Institute which established the "Reciprocity Relation" in the scattering of light and developed experimental methods based on its validity. This relation may be stated as follows. Consider a *parallel beam of plane-polarised light passing horizontally through an isotropic substance*, and let the scattered light be observed in a horizontal direction transverse to the incident beam. The intensity and state of polarisation of the transversely

* This paper reproduces the substance of a lecture delivered to the Indian Academy of Sciences at Bangalore on the 23rd September 1939.

scattered light would evidently depend on the azimuth of polarisation of the incident light. Krishnan's discovery was that, irrespective of the nature, size and shape of the particles of the scattering substance, $H_v = V_h$. These symbols represent respectively, the intensity of the horizontal vibration in the scattered light when the vibration in the incident light is vertical, and the intensity of the vertical vibration in the scattered light when that of the vibration in the incident beam is horizontal. A direct experimental proof of this result is furnished by the arrangement represented schematically in Fig. 1.

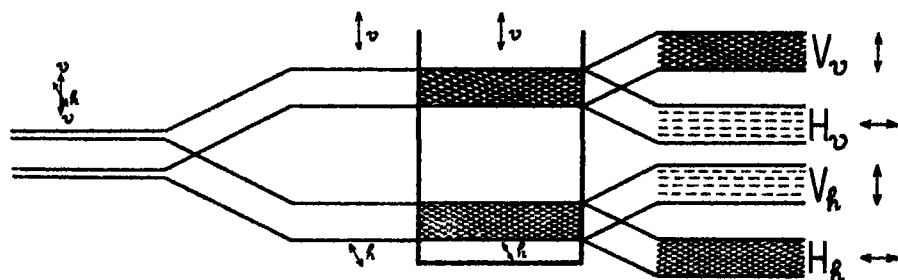


FIG. 1

Demonstration of Reciprocity Principle in Light Scattering

A beam of unpolarised light is divided by means of a double-image prism into two beams of *equal intensity* in which the electric vibrations are respectively vertical and horizontal. These beams enter the observation vessel containing the colloidal substance, and their tracks (which, in general, appear of unequal intensity) are viewed transversely through a double-image prism suitably held. We then see four tracks which may be designated as V_v , H_v , V_h and H_h respectively, the meaning of these symbols being clear from the figure. The equality of intensity of H_v and V_h in all cases is then directly evident to observation. The relative intensity of the four components V_v , H_v , V_h and H_h depends greatly on the size, shape and structure of the particles scattering light.

If the particles are very small, spherical and isotropic,

$$V_v \neq 0, H_v = V_h = H_h \neq 0 \quad (1)$$

If the particles are not small but are spherical and isotropic,

$$V_v \neq 0, H_v = V_h = 0, H_h \neq 0 \quad (2)$$

If the particles are very small but are not spherical and isotropic,

$$V_v \neq 0, H_v = V_h = H_h \neq 0 \quad (3)$$

If the particles are neither small nor spherical and isotropic,

$$V_v \neq 0, H_v = V_h \neq 0, H_h \neq 0. \quad (4)$$

The experimental facts stated in (1), (2), (3) and (4) are readily explained on the basis of the electromagnetic theory of light. The relations stated in (1) follows immediately from the fact that the particle in the conditions stated is equivalent to a simple Hertzian oscillator or electric dipole. The relationships stated in (2) follow immediately from the theory of scattering by spherical isotropic particles developed by Mie (1908). The radiations from the particle may be regarded as the result of the summation of a series of partial vibrations, viz., a first electric, a first magnetic, a second electric, a second magnetic, a third electric, a third magnetic vibration and so on. The first and third electric vibrations, and the second and fourth magnetic vibrations in this sequence give a finite value for V_v and zero values for H_v , V_h , and H_h , while the first and third magnetic vibrations and the second and fourth electric vibrations give a zero value for V_v , H_v , V_h and a finite value for H_h . The superposition of these radiations gives the result stated in (2). The scattering of light by a very small ellipsoidal particle averaged for all orientations of the particle with respect to the field gives the result stated in (3). The relation $H_v = V_h$ is seen to be valid both in case (2) and in case (3). Hence, if the radiation from particles which are neither small nor spherical and isotropic is regarded as a superposition of the types of radiations considered in these two cases, the result $H_v = V_h$ must be valid also in the general case. Krishnan (1938) has given a different argument which also leads to the same result.

3 The Krishnan Effect

From the foregoing considerations, it follows that in the general case $V_h < H_h$. In other words, *if the incident beam is polarised with the electric vibration horizontal, the light scattered transversely would exhibit a partial polarisation in which the horizontal vibration is more intense than the vertical*. This is the Krishnan effect. The actual magnitude of the partial polarisation would be determined by the extent to which radiations of the types envisaged in (2) and (3) respectively enter, in other words by the relation between the size and the optical anisotropy of the particle. In the electromagnetic theory, the amplitude of the first electric radiation is proportional to the cube of the radius of the particle, while those of the first magnetic and the second electric radiations are proportional to its fifth power. Hence, the larger the size of the particle and the smaller its optical anisotropy, the greater would be the partial polarisation and the more readily, therefore, would it be detectable. *Vice versa*, the smaller the particle, and the larger its optical anisotropy, the more difficult of detection would be the partial polarisation of the transversely scattered light. The formulæ of the electromagnetic theory also indicate that the ratios of the amplitude of the higher

partial radiations relatively to the lower ones involve the wave-length of the light. This is evident since the ratios must evidently be dimensionless numbers, such as a^2/λ^2 , a^4/λ^4 , etc., where a and λ are respectively the radius of the particle and the wave-length of the radiation. Hence, for relatively small particles, the effect now under discussion must rapidly become more pronounced as the wave-length of the light is diminished.

4 *A Sensitive Method of Observation*

The partial polarisation of the scattered light referred to above may be readily demonstrated in a variety of cases. A Nicol which can be rotated polarises the light entering the colloid. The track of the beam passing through the observation vessel is viewed transversely through a double-image prism suitably held. It will then be noticed that as the Nicol is rotated and the direction of vibration in the incident beam turns round from the vertical to the horizontal position, the two images of the track seen alter in their relative intensity, the one which is stronger in the first case becomes the weaker in the second case. In other words, $V_v > H_v$ but $V_h < H_h$. The same effect can be shown in a more striking way by viewing the track through a Babinet compensator instead of through a double-image prism. As the polarising Nicol is rotated, the fringes seen in the compensator shift their position, indicating that the partial polarisation of the scattered light alters to a state in which the horizontal component instead of the vertical one is the more intense. As a means of detecting the partial polarisation, this technique is obviously more sensitive than observation through a double-image prism or a measurement of the depolarisation ratio which were the methods employed by Krishnan. A partial polarisation of only a few per cent. is detectable by the Babinet compensator. Hence, the range of the investigation is extended by its use to cases in which the difference of intensity between V_h and H_h is extremely small. Moreover, since the fringes in the Babinet compensator can be photographed, it becomes possible to extend the investigations into the ultra-violet region of the spectrum where, as already remarked, the magnitude of the partial polarisation is expected to become much larger.

The sequence of changes in the appearance of the field of the compensator as the polarising Nicol is rotated may be readily followed. It is evident that, since $V_v > H_v$ and $V_h < H_h$, the fringes would be most marked when the vibrations in the incident light are vertical, their visibility would diminish and reach a minimum value at an oblique setting of the Nicol and increase again to a second maximum when the vibrations are horizontal. The setting of the Nicol at which the compensator fringes have the

minimum visibility would evidently depend on the ratio V_v/H_h . The fringes seen in the compensator appear on a background of uniform illumination due to the unpolarised or "anisotropic" part of the light scattering. The larger this is, the smaller would be the visibility of the fringes for all settings of the Nicol, and in particular at the setting in which the vibrations transmitted by it are horizontal. The sensitiveness of the method therefore diminishes with the increasing optical anisotropy of the particles arising from their non-spherical shape or structure.

5 *Ellipticity of the Scattered Light*

As was shown by Mie, we cannot expect to observe an elliptic polarisation in the light scattered by particles of any size, if the incident light is *unpolarised*. The position would, however, be altered, if the incident light is *plane polarised* in an arbitrary azimuth and the particles of the colloid are spherically symmetric and of uniform size. For, the incident vibration can then be resolved into vertical and horizontal components in a determinate phase relation, and the scattered radiations V_v and H_h arising respectively from these components would also be coherent, the phase relations between them being specifiable and the same for all the particles in the colloid. Unless, therefore, the relationship of phase is one of identity, the resulting radiation would be elliptically polarised. This would be indicated in the Babinet compensator by the position of the fringes which would correspond neither to a vertical nor a horizontal vibration but would be intermediate. In other words, when the Nicol polarising the incident beam is turned round from the vertical to the horizontal, the compensator fringes would shift continuously from one position to the other, remaining visible all the time. An effect of this kind should be easily noticeable when the particles in the medium are of the requisite type, e.g., a cloud of water drops suspended in air or a dilute emulsion of one liquid in another. On the other hand, if the particles in the medium are of such a nature that there is no definite relation of phase between the components V_v and H_v , then no elliptic polarisation should be detectable. In such a case, the compensator fringes would vanish at some particular setting of the Nicol, and re-appear in an altered position when the Nicol is rotated further in either direction.

6 *Applications of the Method*

The sequence of changes observed in the position and visibility of the compensator fringes as the polarising Nicol is turned round is thus closely connected with the structure of the medium scattering the light, and affords an insight into the mechanism of such scattering. In this connection, reference may be made to two very interesting papers by Dr Hans Mueller

(1938) who has discussed the theory of the Krishnan effect from a standpoint which is very different from that set out above

The technique described in the present paper would evidently be applicable to a great variety of cases and should be capable of yielding interesting results. In particular, the increased sensitiveness should enable the Krishnan effect to be looked for even in cases where it is undetectable with the methods previously employed, *e.g.*, colloids of the smallest particle size and even pure liquids. Preliminary work on these lines has been carried out with pure liquids and with liquid mixtures by Mr T A S Balakrishnan and on selected colloidal solutions and emulsions by Mr Darbara Singh. Their results are described in a series of papers appearing in these *Proceedings* under the same title (Parts II, III, IV and V)

Summary

A method is described, based upon the use of a Nicol for polarising the incident beam in any desired azimuth and of a Babinet compensator for observing the transversely scattered light which enables the Krishnan effect to be very conveniently studied. The sensitiveness of the arrangement permits its use for the observation of the effect in cases where the methods previously employed are not delicate enough. It is pointed out that the magnitude of the effect would be enhanced by using ultra-violet radiation, the compensator fringes being recorded photographically. The same arrangement can also be employed for detecting and measuring the elliptic polarisation of the scattered light when the particles scattering the light are uniform and spherically symmetrical. The wide field of utility of the method in the study of light scattering is indicated.

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NEW METHODS IN THE STUDY OF LIGHT SCATTERING

Part II Pure Liquids

BY T A S BALAKRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

It is well known that when a beam of unpolarised light traverses a column of dust-free liquid, the track of the beam observed in a transverse direction exhibits a partial polarisation, the extent of this depending on the liquid employed. The so-called depolarisation factor ρ which is the ratio of the intensities of the vibration components respectively parallel and perpendicular to the plane of observation in the transversely scattered light depends on the liquid under study. It is relatively small for organic liquids of the aliphatic class, e.g., carbon tetrachloride or ethyl ether, and much larger for liquids of the aromatic class, e.g., benzene. If the beam of light is polarised before entry into the liquid, the depolarisation ratio is altered and then depends on the azimuth of polarisation of the incident light. According to R. S. Krishnan (1935) the following general equation is valid for all isotropic media

$$\rho_u = (1 + 1/\rho_h) / (1 + 1/\rho_v). \quad (1)$$

In this formula ρ_u , ρ_v , and $1/\rho_h$ represent the values of the depolarisation ratio, when the incident beam is respectively unpolarised and polarised with vibrations perpendicular and parallel to the plane of observation. According to present knowledge, in the case of pure liquids,

$$\rho_h = 1 \quad \text{and therefore} \quad \rho_u = 2\rho_v / (1 + \rho_v) \quad (2)$$

If the incident light be polarised with the vibrations making an angle θ with the vertical, the depolarisation ratio ρ_θ in the general case is, according to R. S. Krishnan (1939)

$$\rho_\theta = (1 + \tan^2 \theta / \rho_h) / (\tan^2 \theta + 1/\rho_v) \quad (3)$$

From formula (3), it follows that

$$\rho_v = \rho_{0^\circ}, \rho_u = \rho_{45^\circ}, \rho_h = 1/\rho_{90^\circ} \quad (4)$$

In the particular case when $\rho_h = 1$, formula (3) reduces to

$$\rho_\theta = \rho_v / (\rho_v \sin^2 \theta + \cos^2 \theta) \quad (5)$$

The question arises whether ρ_h in the case of liquids is *exactly* equal to 1. Since the dimensions of molecules are very small compared with the wavelength, we may expect this to be the case provided that the scattering of light in a liquid may, as with gases, be assumed to be due to the individual molecules. But since a liquid is a dense aggregate of molecules, the latter assumption is questionable. Actually, the scattering of monochromatic light in a liquid is shown by spectroscopic research to be of several distinct kinds. Firstly, we have the Raman lines exhibiting relatively large frequency shifts. As the intensity of these lines relatively to the rest of the scattering is small in liquids, we shall not consider them further in the present connection. Secondly, we have the "wings" appearing in the spectrum on either side of the parent line in the incident radiation. This is due to hindered molecular rotation and is a depolarised radiation for which $\rho_h = 1$. Thirdly, we have the scattering by longitudinal sound waves appearing as a Brillouin doublet enclosing the parent line in the spectrum. Theory and experiment appear to agree in indicating that this radiation is completely polarised, i.e., $H_v = V_h = H_h = 0$. Finally, we are left with the scattering of unmodified frequency, represented by an undisplaced line in the spectrum. This has been shown by B. D. Saxena (1938) and by Sunanda Bai (1941) to be polarised partially, but to varying extents for different liquids. The origin of this unmodified scattered radiation in liquids has not yet been fully elucidated, but it has been suggested that it may be connected with the quasi-static structure of the liquid, and that it is probably analogous to the unmodified scattered radiation observed with amorphous solids or glasses. It is conceivable that this scattering may be due, in part, to relative large clusters of molecules, in which case we may expect that $\rho_h < 1$. Whether this is actually so or not can only be decided by experiment.

That ρ_h is practically unity in the case of pure liquids has long been known as a fact of observation. It is evident, therefore, that very sensitive methods would be required to exhibit any departure from this relation, the ordinary method of measuring depolarisation being inadequate for the purpose. In Part I of this series of papers, Sir C. V. Raman (1941) has suggested the use of a Babinet compensator or other sensitive polariscope for the detection of the effect. The purpose of the present investigation was to test out this idea, using a Babinet compensator to decide whether or not ρ_h for pure liquids is unity. The results of a *preliminary* investigation with three pure liquids, namely, carbon tetrachloride, benzene and ethyl ether are recorded in the paper.

2 Experimental Arrangements

A pyrex glass cross of one-inch diameter with its four arms of length about 3 inches was taken. The fourth arm opposite the observation end was drawn out and bent up in the shape of a horn. The tip of the horn was connected to a glass flask which was filled with the liquid under investigation. The liquid was distilled over into the cross and then washed back into the flask about six or seven times so as to get it free of dust. After each distillation the liquid in the cross was tested with a strong beam of sunlight for any specks of dust. After the last distillation the cross was sealed off. It was blackened thoroughly on the outside except for three flat pyrex glass windows and then mounted in position. The observations were made in a dark cabin in the wall of which there was an aperture letting in a beam of sunlight reflected from a single-mirror Foucault heliostat. A Dallmeyer lens of focal length 12" provided with a diaphragm to vary the aperture was fixed to the wall of the cabin in the path of the beam of sunlight and served to focus the incident illumination. Immediately after the lens, a glass cell with parallel plane end-pieces containing a solution of alum was placed to cut off the heat rays. Next to the cell was mounted a Nicol provided with a graduated circle which could rotate about the incident beam and thus cause the light to be polarised in any desired azimuth. The light after passing through the Nicol was focussed at the centre of the cross. To view the light transversely scattered by the liquid, the Babinet compensator was placed with its principal plane inclined at 45° to the plane of observation, in which position the compensator is most sensitive. The scattered light then passed through another Nicol oriented so as to transmit vibrations which had their electric vector horizontal. An eyepiece was used to make the visual observations. The eyepiece was removed and substituted by a camera with a lens having a maximum aperture of $f/4.5$ for taking photographs of the pattern of fringes formed in the field of vision. A series of filters ranging from a red filter to Wood's glass was used to study the phenomena at different wave-lengths. The photographs were taken on Selochrome or Ilford HP2 plates and developed with the Ilford Process plate developer.

There are several likely sources of error in the experiment. The first is the possibility of dust particles in the liquid giving a polarised scattering. This was eliminated by careful and repeated distillation. Secondly, the angle of convergence of the beam introduces some complications. This was avoided by making visual observations with continually reduced apertures. Thus when the apertures were reduced to as low a value as $f/22$, the liquids under investigation continued to exhibit the phenomena. The convergence

error for this aperture is very low and of the order of 0.03%. A third source of error lay in the diffuse scattering of light by the background. This was completely avoided by eliminating all extraneous light other than that passing through the cross, and the beam was kept so narrow that it did not impinge on the side of the cross anywhere in its track. The horn of the cross along with the thick coating of black everywhere on the outside combined to give a perfectly dark background over which the track of the incident light could be seen clearly. A series of diaphragms and screens completely cut out all extraneous light and there were similar diaphragms on the observation side of the cross in the path of the scattered light. The greatest care was exercised in seeing that only light scattered by the liquid at the centre of the cross was transmitted to the Babinet compensator and that no extraneous diffuse light had access to it.

3 Results

The experiment was first conducted visually with the eyepiece mounted after the analysing Nicol in the path of the scattered light. When the incident light was polarised with its electric vector perpendicular to the plane of observation, the fringes in the Babinet's compensator appeared very brightly in the field of vision. The cross wire in the Babinet, consisting of a narrow fibre of silk stretched between the two quartz wedges, appeared on the central dark band. Since white light was used, coloured fringes were visible at the edges of the field. In the centre, however, there were three dark bands separated by white bright bands. Slowly turning the Nicol, the vibrations in the incident light were altered from the vertical to the horizontal and then further turned till they again became vertical. When this was done gradually, it was found that the fringes lost intensity, vanished completely and then reappeared again forming the same pattern as before. Midway when the vibrations were horizontal, there was a faint trace of illumination, and the question whether the fringes were present there or not could not be settled visually. The device of oscillating the Nicol rapidly about the position where the illumination was a minimum was then tried, and it was found that the fringes instead of disappearing completely showed up in a shifted position, the crosswire appearing on a bright band instead of on a dark band. Each time the Nicol was flicked about ten degrees on either side of the position at which the illumination in the field of the compensator was a minimum, the bands momentarily shifted their position and then came back to their original position. Thus the reversal of polarisation and the existence of fringes were both made clearly visible to the naked eye by this device. This reversal of polarisation was found to persist even at small apertures, up to about $f/22$. The eyepiece was now replaced by the camera and a series of

photographs taken for successive positions of the polarising Nicol, separated by one degree from the preceding position. Photographs of the fringe pattern formed at the Babinet compensator were taken for a range of ten degrees on either side of the horizontal position of the polarising Nicol. It was found that the fringe pattern shifted from one position to another within the space of a degree and that the fringes were very faint; they in fact almost disappeared at the position of transition. In the next setting of the Nicol separated by one degree from the position of transition, the photograph reveals the crosswire to be on a bright band. After this, the fringes continue to gain in intensity and become clearest when the vibrations in the incident light are horizontal. With further rotation, the fringe system loses intensity, till at the point of transition on the other side, they nearly vanish. In subsequent positions, the crosswire is seen on the dark band. If the rotation is carried on to make the vibrations in the incident light vertical, the fringe system is of maximum intensity.

The experiment was first conducted with carbon tetrachloride and five pictures are furnished in Fig. 1, Plate XI. The crosswire is on a black band for the first picture and the vibrations in the incident light are vertical. The reading on the graduated scale of the Nicol is 270° . The second position indicates the position of transition with the Nicol reading at 185° . Here the fringes have lost considerably in intensity and the crosswire is just visible over the black band. In the third picture the crosswire has shifted to a bright band and can be seen with two faint dark bands on either side. The Nicol reading for this position is 180° . The other two pictures show respectively the transition occurring at 175° and the fringe system with the vibrations in the polarised light vertical. The Nicol reading for the last picture is 90° .

The experiment was repeated with benzene. The reversal could not be observed visually. There was a certain quantity of general illumination in the field of vision and the fringes could not be seen when the vibrations in the incident light were horizontal. The field of view of the Babinet compensator and the analysing Nicol was photographed for successive positions of the Nicol. Among the five pictures furnished in Fig. 2, Plate XI the fringes are seen in two where the crosswire is on a dark band, but not in the other three. The corresponding readings for the settings of the polarising Nicol are given alongside.

The dependence of the polarisation of the scattering of light upon the wavelength was studied when the polarising Nicol was transmitting only horizontal vibrations. This was done by interposing suitable filters in the

path of the scattered light Red, yellow, blue, violet and Wood's glass filters were used successively and a series of pictures with these filters are reproduced in Fig 3, Plate XII. In all these cases the crosswire appears on a bright band and the reversal of polarisation can be seen more clearly with decreasing wavelength

The experiment was repeated with ethyl ether which was also carefully distilled into a pyrex glass cross. Four pictures are reproduced in Fig 4, Plate XII They were also taken with the polarising Nicol oriented so as to transmit horizontal vibrations and with red, yellow, blue and violet filters The reversal is exhibited by ether in a striking manner and the visibility of the fringes improves markedly when the violet filter is used for photographing the pattern of fringes

In the case of benzene it was found that the fringes refused to register when the incident light had its vibrations horizontal even though the Wood's glass filter was used All that could be obtained on the photographic plate was a certain quantity of general illumination and the dark crosswire. The failure to observe the effect with benzene is not surprising as benzene has a depolarisation ratio of 42% while those of carbon tetrachloride and ether are respectively 6% and 8.5%. The great intensity of the depolarised orientation scattering in the case of benzene would naturally overpower a feeble polarised scattering even if it were present

The author desires to record his grateful thanks to Professor Sir C. V Raman, F.R.S., for suggesting the problem and for valuable help during the course of the investigation His thanks are also due to Dr C S Venkateswaran for kind advice and assistance.

4 Summary

Till now, it has been assumed that the light scattered in dust-free liquids is completely unpolarised when the incident light is polarised with its vibrations in the plane of observation Using a Babinet compensator with an analysing Nicol oriented so as to transmit vibrations in the plane of observation, the author has established the presence of a feeble partial polarisation in the scattered light when the incident light is polarised as stated above The presence of the feeble polarisation is shown by the appearance of fringes when the scattered light is viewed through the Babinet compensator Photographs showing these fringes with carbon tetrachloride and with ether are reproduced. The fringes are, however, not observable in the case of benzene, being apparently masked by the much more intense unpolarised scattering

Reading
of
Polarising
Nicol

90



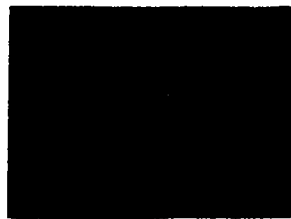
175



180



185



270°



FIG 1
Carbon tetrachloride

Reading
of
Polarising
Nicol

172



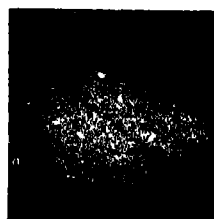
176



180



184



188°



FIG 2
Benzene

Light Scattering in liquids observed through a Babinet Compensator

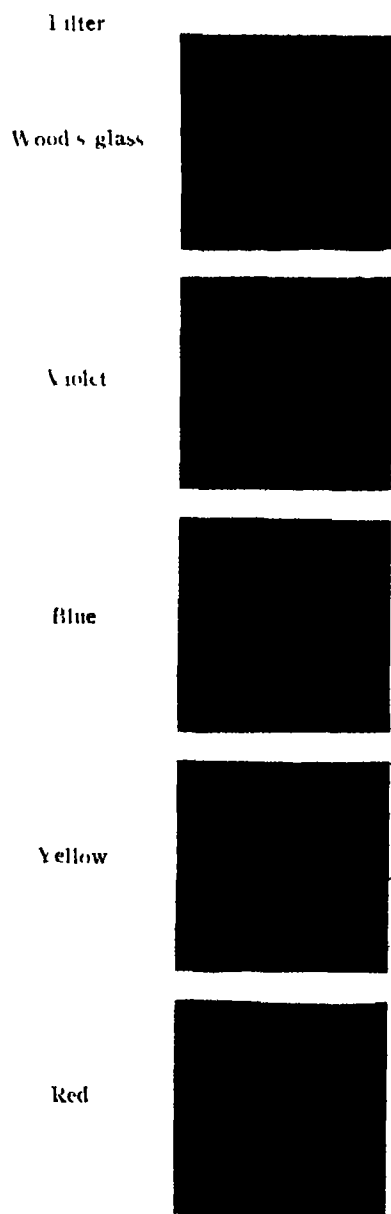


FIG 3
Carbon tetrachloride

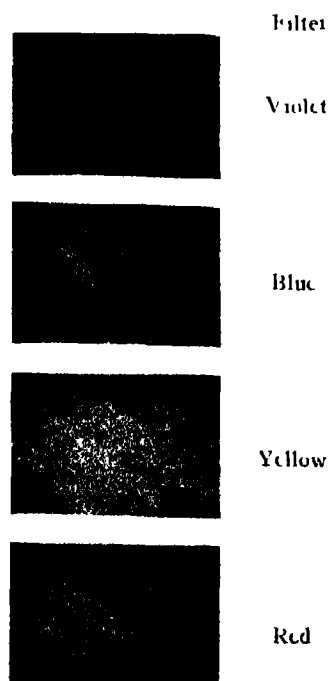


FIG 4
Ethyl ether

Light Scattering in Liquids observed through a Babinet Compensator

present in the case of this liquid. The fringes noticed with carbon tetrachloride and ether become the more striking as the wave-length of the incident radiation is decreased.

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STUDIES ON THE RAMAN EFFECT IN SINGLE CRYSTALS OF POTASSIUM NITRATE

BY T M K NEDUNGADI

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

POTASSIUM NITRATE is well known to be chemically similar to sodium nitrate but crystallographically isomorphous with aragonite. Its structure bears the same relation to sodium nitrate as aragonite bears to calcite. Detailed studies have already been made on the Raman effect in sodium nitrate (Nedungadi, 1939) and calcite (Bhagavantam, 1940) with particular reference to the effect of crystal orientation on their spectra and these have yielded useful information regarding the dynamics of these crystals. By extending the study to potassium nitrate we can follow up the changes introduced in the spectrum due to change of symmetry and with the consequent change of environment of the NO_3^- ion. Further, a study of the thermal effects on the spectrum of this crystal is interesting, because it undergoes a polymorphic transformation at 129°C . from orthorhombic to trigonal symmetry. We might expect to find important changes for the Raman lines, particularly for those due to lattice oscillations, following the transformation.

Research on the Raman effect in potassium nitrate has been mostly confined hitherto to the studies of the crystal powder, of the melt and of the aqueous solution with a view to find out the changes in the characteristic frequencies of the NO_3^- ion due to change of state. Among the authors who studied the spectrum of the crystal previously, namely, Krishnamurti (1930), Menzies (1929), Barr (1929), Nisi (1931) and Anantakrishnan (1937), Nisi alone used a single crystal for his study. The frequency shifts observed by him are 31, 51, 84, 711, 1049 and 1344. Out of these the first three lines are attributed to the characteristic oscillations of the crystal lattice and the last three to the internal oscillations of the NO_3^- ion. Line 1049 corresponds to ν_0 the symmetrical breathing oscillation, while the lines 711 and 1344 are due to ν_3 and ν_2 the two doubly degenerate frequencies of the NO_3^- ion. However, Anantakrishnan has observed that the line 1344 is really a doublet with frequency shifts 1341 and 1360. The frequency at 830 due to the oscillation of the N atom along the symmetry axis which is inactive in Raman effect for

the free ion has not been observed hitherto, though theory indicates that it should appear in the spectrum of this crystal. Further, the crystal aragonite yields six low frequency lattice oscillations (Rasetti, 1932) and it is natural to expect corresponding lines in potassium nitrate also. In these circumstances, a study of the dependence of the Raman lines on the temperature and also on the effect of crystal orientation has been made, and the results so far obtained are reported in the following pages.

2 *Experimental*

As potassium nitrate undergoes a polymorphic transformation between its melting point and the room temperature, it is impossible to grow single crystals from melts of the substance, as these while being cooled through the transformation temperature break up to form polycrystalline masses. The crystals used for the present study were, therefore, grown from solution. Great care had to be exercised in adjusting the saturation of the solution and maintaining the constancy of temperature of the crystallisation room in order to obtain fairly large clear single crystals. Crystals measuring $1.5 \times 1 \times 0.8$ cm were obtained in the present case. The experimental arrangements used for the studies were practically the same as were described in some of the earlier papers of the author. However, the polaroid used hitherto for polarising the incident light was replaced by a large aperture (1 inch square) Ahren's nicol. The disadvantages of using a polaroid are threefold—Firstly, its polarising power in the $\lambda 4358$ region is not complete but only 90%. Secondly, it cuts off $\lambda 4046$ to a large extent and hence observations on the Raman frequencies excited by this line cannot be made. Thirdly, the absorption of $\lambda 4358$ itself is considerable. All these defects of the polaroid could be avoided by using a nicol, though this involves the sacrifice of part of the incident light intensity by the limited aperture of the nicol. For accurate quantitative results the incident light has to be strictly a parallel beam. This necessitates the using of a point source of light at the focus of a lens. However, practical considerations of the intensity of the incident beam for reasonable times of exposure, necessitate the use of a fairly large aperture condensing lens to focus the light from a vertical arc on to the crystal. This at present is an unavoidable evil. The semi-convergence angle thus introduced in the present study was about 10° .

3 *Raman Frequencies in the Spectrum*

Fig. 1 is a clear spectrum of the crystal recorded with the unpolarised light incident along the *b*-axis and the scattered light observed along the *c*-axis. The frequencies observed in a detailed analysis of this spectrogram are given in Table I.

TABLE I

Raman lines	Excitation	Raman lines	Excitation	
52	<i>k, l, e</i>	714	<i>k, e</i>	<i>k</i> — λ 4046 5 Å
82	<i>k, l, e</i>	1050	<i>k, l, l, e</i>	<i>l</i> — λ 4077 8 „
100	<i>k, e</i>	1343	<i>k, e</i>	<i>l</i> — λ 4347 5 „
126	<i>k, e</i>	1361	<i>k, e</i>	<i>e</i> — λ 4358 3 „
143	<i>e</i>			

The following features of the spectrum may be specially noted (1) Three new lines 100, 126 and 143 due to lattice oscillations have been recorded for the first time (2) The two lattice lines 52 and 82 are very intense, the latter being much stronger than even the symmetrical oscillation 1050 of the NO_3^- ion (3) The line at 1350 due to the degenerate oscillation is a clearly resolved doublet consisting of sharp lines at 1343 and 1361. However, the other degenerate oscillation at 714 remains a sharp line. The aggregate intensity of the 714 line is roughly equal to the sum of the intensities of the separate components of the doublet at 1350 (4) No line due to the ν_1 oscillation of the NO_3^- ion is recorded at about 830 as in the case of aragonite. A lattice line at 31 with zero intensity reported by Nisi appears to be doubtful as it is not noticed in any of the strongly exposed plates of the present author in spite of the fact that three weak new lattice lines have been clearly recorded.

Bhagavantam (1941) has shown from group theoretical considerations that orthorhombic crystals of aragonite and KNO_3 should yield 18 Raman lines due to lattice oscillations. Six have been recorded by Rasetti for aragonite using the λ 2537 excitation of the mercury arc. The new lattice lines observed in KNO_3 are thus seen to be a necessary consequence of the orthorhombic symmetry of the crystal. That the line 82 in KNO_3 corresponds to the line 185 in NaNO_3 and is due to the tilting oscillations of the NO_3^- ions in the lattice will be shown in a later section. The great intensity of the lattice lines 52 and 82, particularly of the latter, can be easily observed in the spectrogram. In the paper of the present author referred to earlier, it has been shown that the intensities of the symmetrical oscillation and of the tilting oscillation of the NO_3^- ion are inversely proportional to their frequencies and that as a consequence, in the case of NaNO_3 , where the corresponding lines are at 1065 and 185, the latter should be stronger of the two even when the crystal is oriented in a manner most favourable for recording the 1065 line strongly.

In the case of KNO_3 the tilting oscillation has a much lower frequency, nearly half that of NaNO_3 , whereas the symmetrical oscillation of the NO_3^- ion has practically the same value. Hence, it is but natural to expect that the line 82 should be stronger than the line 1050. The doubling of the degenerate line 1350 should be a consequence of the NO_3^- ion which has a threefold axis of symmetry going into a less symmetrical orthorhombic lattice which has no axis of symmetry of an order higher than two. Further, it is to be expected that the line 714 would also split up into a doublet as the modes of oscillation of the NO_3^- ion giving rise to both these lines are confined to the plane of the ion and are fundamentally similar. That this line actually consists of two separate components is shown by polarisation studies. The interesting observations on these and on the relative behaviour of the components of the doublet at 1350 with varying orientation of the crystal even when the incident light is unpolarised will be described in a later section.

The ν_1 frequency of the NO_3^- ion corresponds to a vibration of the N atom perpendicular to the plane of the ion. As it involves only a change in the electric moment of the ion and not a change in its polarisability this oscillation is inactive in Raman effect but active in infra-red. When the ion goes into the orthorhombic crystal lattice, the change in the selection rules enables the appearance of this oscillation in Raman effect theoretically. Special attempts were made by the present author to record this line in KNO_3 but without success. Spectra in which even the degenerate lines are intense do not show any indication of this line. It appears, therefore, that the polarisability charges accompanying this oscillation caused by the influence of the neighbours on any NO_3^- ion are quite inappreciable. The corresponding line at 852 reported by Rasetti in aragonite is also apparently very feeble as it cannot be detected in the spectrum reproduced by him in his paper in spite of the fact that all the other lines he reports are easily visible in the same.

4. Effect of Temperature on the Raman Spectrum

Spectra of a single crystal of potassium nitrate were taken at 25°, 120°, 170° and 290° C. For a comparison of the effects produced by change of state, a spectrum of the substance in the molten state (m.p. 334° C) was also recorded. With a uniform temperature field inside the heater the crystal could be heated gradually beyond the transformation temperature (129° C) without fracture. Nevertheless, in the process of cooling it invariably cracked up below the transition temperature into micro-crystals. The frequency shifts of the crystal measured at the room temperature, at 290° C, as also those in the melt are recorded in Table II. Figs. 2 *a* and 2 *b* are the spectra taken with a Hartmann diaphragm at temperatures 25° and 120° C. respectively.

TABLE II

	Lattice Oscillations				ν_s	ν_0	ν_a
Crystal at 25° C	52	82	100	126	714	1050	1343 1361
Crystal at 290° C	.			.	710	1047	1330 to 1365
Molten 350° C	Wing extending up to 95 cm. ⁻¹				710	1045	1265 to 1420

A significant observation made in the present study is that the two lattice oscillations with frequency shifts 100 and 126 and presumably also the one at 143 broaden out and practically vanish at 120° C. as may be seen in Figs 2 *a* and 2 *b*. It is clear that these lattice lines which are absent in the case of sodium nitrate are a consequence of the lower symmetry of potassium nitrate crystal. Hence, it is natural to expect that when the NO_3^- ion finds itself in the field of trigonal symmetry, these new lines should disappear. The observation is analogous to that made by the author in the case of α -quartz in which a particular oscillation of frequency shift 207 vanishes at the temperature of transition to β -quartz (Nedungadi, 1940). This observation in potassium nitrate also confirms the idea that a polymorphic transition in crystals involving an increase of its symmetry is characterised by the disappearance of certain oscillations of the lattice.

There is general similarity, as might be expected, between the variation with temperature of the Raman lines of sodium nitrate and potassium nitrate. The behaviour of the lattice lines 52 and 82 is generally similar to that of 98 and 185 respectively of sodium nitrate. Nevertheless, the line 82 broadens much faster than the corresponding line of sodium nitrate. Even at 170° C the line is a very broad band. Greater details regarding the behaviour of these lines could not be made out due to the halation round the Rayleigh line developed at high temperatures.

As regards the internal oscillations, the rate of broadening of the lines with temperature is very slow. However, even at 120° C the two lines 1343 and 1361 constituting the doublet have broadened out and consequently appear weaker though the doublet structure is still discernible. On the other hand at 170° C (which is above the transition temperature) these two component lines have broadened out so much as to merge into one another and appear as one band. At 290° C. this line broadens further and extends over 35 cm⁻¹ while the line 714 still remains comparatively sharp. The frequency shifts for these internal oscillations remain appreciably unaltered up to 290° C.

In the melt the lines due to internal oscillations are much broader than even in the crystal at 290°C but the change in the frequencies due to change of state is not so conspicuous as in the case of sodium nitrate. The degenerate oscillation at 1350 is very broad in the melt and extends over 150 cm^{-1} . It is noteworthy that the wing accompanying the Rayleigh line extends much less in KNO_3 compared to NaNO_3 , though the distribution of intensity in the wing is similar in both substances. Some of these characteristics of the molten substance have been clearly recorded previously by Moses (1939).

5 *Effect of Crystal Orientation on the Raman Spectrum*

As usual in studies on the orientation effect on the spectrum of the light scattered by crystals in a transverse direction, we designate the direction of the incident beam by OX and of observation of the scattered light by OY, OZ being perpendicular to both. For a biaxial crystal with the principal optical directions* α , β and γ , it can be easily shown that we can obtain 54 different spectra for different orientations of the crystal with respect to the directions of incidence and observation and for different states of vibration of the incident and scattered light. This includes 6 spectrograms when the incident light is unpolarised and the scattered light is not analysed, 12 when the incident light is unpolarised and the scattered is analysed, 12 when the incident light is polarised and the scattered light is not analysed and 24 when the incident light is polarised and the scattered light is also analysed. It is obvious that the last 24 are the most important as they comprise the results of the rest also. It should be pointed out here that the potassium nitrate crystal, though orthorhombic, exhibits pseudo-hexagonal symmetry; the optical anisotropy in the $\beta\gamma$ plane is extremely small as may be seen from the values of the refractive indices $\gamma=1.513$, $\beta=1.512$, $\alpha=1.336$. This is, indeed, due to the fact that the NO_3^- ions in this crystal are all oriented with their planes perpendicular to the α -axis. Owing to this fact, only 12 spectra out of the 24 mentioned above were taken in the present study. These 12 spectra closely correspond to those of sodium nitrate studied earlier with the α -axis substituted for the optic axis of the latter. These spectrograms are reproduced in three groups of four each (a , b , c and d) in Figs. 4, 5 and 6 corresponding to the orientations of the α -axis along OX, OY and OZ respectively. Further, three spectra recorded with unpolarised incident light for the above orientations of the α -axis are also reproduced in Fig. 3 (a , b and c). The diagram of the orientation of the NO_3^- ion for the different spectrograms along with the usual notations for the nature of the vibrations of the incident and scattered light are

* In the case of KNO_3 these coincide with the c , b and a crystal axes respectively.

also given by the side of the figures. The intensities of the lines measured by the usual method of microphotometry (after making the necessary correction for the spectroscope error in the case of polarisation studies) are recorded in Tables III and IV. The values are relative to the most intense line in any particular spectrogram taken as 100. It should be pointed out here that owing to the feebleness of the lines due to the degenerate oscillations (compared with the intense lattice lines, sufficiently long exposures were not given to record the former lines in all cases as they would involve the sacrifice of the details regarding the lattice lines due to over-exposure.

An inspection of the figures in the Plates shows that there is a general similarity in the behaviour of the Raman lines with orientation in sodium and potassium nitrates. Comparing Figs 3 *a*, 3 *b* and 3 *c* when the incident light is unpolarised and the scattered light is not analysed, the most notable feature is that while the low frequency lattice oscillations are fairly of uniform intensity in all the three, the degenerate oscillations, and in particular, the line 1050 due to the symmetric oscillation of the NO_3^- ion, are very weak in the third spectrogram when the plane of ion coincides with the plane containing the incident and scattered rays. This fact can be seen also when the incident light is polarised with vibrations perpendicular to the direction of observation, if we compare the aggregate intensities of the *a* and *b* components in each of the Figs 4, 5 and 6. These facts show clearly as in the case of sodium nitrate that the polarisation due to an incident light vector perpendicular to the plane of the NO_3^- ion is much less than that in the plane

Another observation is that the low frequency lattice oscillations disappear when the internal oscillations appear strongly in the spectrum of the light scattered along the *a*-axis when the incident light vector is in the plane of the NO_3^- ion (Figs 5 *a* and 5 *b* taken together). However, the reverse is true for the same orientation of the crystal when the incident light vector is perpendicular to this plane (Figs 5 *c* and 5 *d* taken together). This reciprocal behaviour can also be seen in the rest of these 12 spectrograms taken with the incident light polarised and the scattered light analysed. This spectral behaviour is strictly true for the lattice lines 82, 100 and 126 but not for the line 52 in all cases. However, it is generally clear that the changes in polarisability giving rise to these low frequency lines arise in a manner fundamentally different from those of the internal oscillations.

A particularly striking divergence in the behaviour of the lines 52 and 82 is that the former appears extremely feeble when the incident light vector is perpendicular to the plane of the NO_3^- ion and also to the direction of observation (Figs 6 *a* and 6 *b*) while the latter line appears strongly in the

TABLE III
Incident Light Unpolarised

No	β -axis oriented along	α -axis oriented along	Vibrations of the incident light vector in	Intensities of Raman lines								
				52	82	100	126	143	714	1050	1343	1361
1	OZ	OX	YZ plane	45	100	13	15	4	12	70	7	7
2	OX	OY	YZ plane	50	100	12	17		12	75	6	6
3	OX	OZ	YZ plane	50	100	14	15		7	18	7	4

 TABLE IV
Incident Light Polarised

No	β -axis oriented along	α -axis oriented along	Vibrations of the incident light vector along	Intensities of components of Raman lines									
				52		82		100		126		714	
				OX	OZ	OX	OZ	OX	OZ	OX	OZ	OX	OZ
1	OZ	OX	OZ	30	4	100	7	10	.	14		2	4
2	OZ	OX	OY	50	2	100	10	6	.	10		2	
3	OX	OY	OZ	3	3	8	8				6	1	6
4	OX	OY	OY	16	48	100	88	9		6		6	
5	OX	OZ	OZ	5	5	100	7	6		9			
6	OX	OZ	OY		54	4	100				3	3	

OX component Further the line 52 is very strong in the OZ component and weak in the OX component in the light scattered perpendicular to the NO_3 plane when the incident light vector is parallel to the direction of observation (Figs 5 c and 5 d). However, the behaviour of this line is quite similar to the line 82 in all the other cases studied. The polarisation behaviour of the two lattice lines 100 and 126 is the same as that of the line 82 in all the cases where they were recorded.

Attention has already been drawn to the fact that the degenerate oscillation ν_2 of the NO_3^- ion appears as a doublet with frequency shifts 1343 and 1361 in this crystal. The behaviour of the split components with crystal orientation is noteworthy. Comparison of Figs 3 a, 3 b and 3 c shows that with incident unpolarised light, the line 1361 practically vanishes when the plane of the NO_3^- ion coincides with the plane containing the incident and scattered beams (Fig 3 c) while the line 1343 appears fairly strong in the same. Further, in the spectrum of the light scattered along the α -axis for incident light polarised with vibrations in the plane of the NO_3^- ion, the 1361 line appears only in the OZ component while the line 1343 appears in the OX component (Figs 5 a and 5 b). These and other observations on the component lines of this doublet prove, as has been shown in the next section, that the line 1361 is due to a symmetrical oscillation of the crystal and the line 1343 to an anti-symmetric one. In a similar manner, polarisation studies show clearly that the line 714, though it appears in the spectrum as a single line, is due to the superposition of a symmetric and an antisymmetric oscillation of the crystal. A careful examination of the negatives seems to indicate that the component due to the symmetric oscillation has a frequency corresponding to the low frequency edge of the line and that due to the antisymmetric oscillation to its high frequency edge (in Figs 5 a and 5 b for example). This behaviour stands in contrast to that of the doublet at 1350 where the symmetric oscillation has a higher frequency than the antisymmetric one.

6 Discussion of Results

According to Placzek (1934) the activity in Raman effect of any crystal vibration is indicated by six components ϵ_{ii} and ϵ_{ik} of the change of polarisability tensor. The surviving tensor components for any vibration can be derived from a knowledge of the symmetry properties of the vibrations and of the crystal. Accordingly an orthorhombic crystal can only have two types of vibrations (1) symmetric and (2) antisymmetric (Saxena, 1940). The symmetric oscillations are characterised by the fact that the diagonal terms of the tensor persist and the transverse terms disappear. Thus the selection rules for this type of vibration is

$$\epsilon_{xx} \neq \epsilon_{yy} \neq \epsilon_{zz}; \epsilon_{ik} = 0.$$

The antisymmetric oscillations are characterised by the fact that the diagonal terms are always zero. Further, these can be divided into three types —

- (1) Vibrations antisymmetric to $C_{\alpha\sigma_\beta}$, $C_\alpha C_\beta$, or $\sigma_\alpha, \sigma_\beta$
by only $\epsilon_{\alpha\beta} \neq 0$, the rest being zero
- (2) Vibrations antisymmetric to $C_\gamma\sigma_\alpha$, or $C_\gamma C_\alpha$, or $\sigma_\gamma\sigma_\beta$
by only $\epsilon_{\beta\gamma} \neq 0$, the rest being zero
- (3) Vibrations antisymmetric to $C_\gamma\sigma_\beta$, or $C_\gamma C_\beta$, or $\sigma_\gamma\sigma_\beta$
by only $\epsilon_{\beta\gamma} \neq 0$, the rest being zero

Experimentally, these surviving tensor components for the various vibrations can be observed by studies on the Raman spectra of oriented crystals. The following equations determine the intensities of the various components in any general case

$$\begin{aligned} P_x &= \epsilon_{xx} E_x + \epsilon_{xy} E_y + \epsilon_{xz} E_z \\ P_y &= \epsilon_{yx} E_x + \epsilon_{yy} E_y + \epsilon_{yz} E_z \\ P_z &= \epsilon_{zx} E_x + \epsilon_{zy} E_y + \epsilon_{zz} E_z \end{aligned}$$

where p_x and E_x stand for the x -components of the induced moment and of the incident light vector respectively. x, y and z signify the directions OX, OY and OZ respectively. For an incidence along OX, the components of the scattered radiation are along OX and OZ. Since ρ the depolarisation ratio $= \frac{p_z^2}{p_x^2}$, that for an incident electric vector along OZ, $\rho = \frac{\epsilon_{zz}^2}{\epsilon_{xx}^2}$ and for an incident electric vector along OY, $\rho_y = \frac{\epsilon_{yz}^2}{\epsilon_{yy}^2}$.

In a biaxial crystal where the axes α, β and γ of the optical polarisability ellipsoid have different magnitudes, for a particular orientation of the γ -axis say along OZ, the α -axis can be either oriented along OX or along OY. In the former case, for an incident electric vector along OZ, $\rho = \frac{\epsilon_{\alpha\gamma}^2}{\epsilon_{\gamma\gamma}^2}$ and for an electric vector along OY, $\rho = \frac{\epsilon_{\beta\alpha}^2}{\epsilon_{\beta\gamma}^2}$. The corresponding values for the latter case are

$$\rho = \frac{\epsilon_{\gamma\beta}^2}{\epsilon_{\gamma\gamma}^2} \text{ and } \rho = \frac{\epsilon_{\alpha\beta}^2}{\epsilon_{\alpha\gamma}^2}.$$

The γ -axis can be also oriented along OX and OY. The polarisation and the total intensities for various orientations of the crystal thus possible are collected in Table V.

However, to determine the surviving tensor components for any vibration it is not necessary to study fully all the possible orientations of the crystal

TABLE V

Serial No	Orientation of the crystal	Depolarisation			Total intensities		
		Incident light vector along OZ	Light vector along OY	Unpolarised light	Light vector along OZ	Light vector along OY	Unpolarised light
1	α along x						
	$\gamma - y$	$\frac{\epsilon_{\beta}^2}{\epsilon_{\beta\beta}^2}$	$\frac{\epsilon_{\gamma\alpha}^2}{\epsilon_{\gamma\beta}^2}$	$\frac{\epsilon_{\beta\alpha}^2 + \epsilon_{\gamma\alpha}^2}{\epsilon_{\beta\beta}^2 + \epsilon_{\gamma\beta}^2}$	$\epsilon_{\beta\alpha}^2 + \epsilon_{\beta\beta}^2$	$\epsilon_{\gamma\alpha}^2 + \epsilon_{\gamma\beta}^2$	$\epsilon_{\beta\alpha}^2 + \epsilon_{\beta\beta}^2 + \epsilon_{\gamma\alpha}^2 + \epsilon_{\gamma\beta}^2$
	$\beta - z$						
2	$\alpha - x$						
	$\gamma - z$	$\frac{\epsilon_{\gamma\alpha}^2}{\epsilon_{\gamma\gamma}^2}$	$\frac{\epsilon_{\beta\alpha}^2}{\epsilon_{\beta\gamma}^2}$	$\frac{\epsilon_{\gamma\alpha}^2 + \epsilon_{\beta\alpha}^2}{\epsilon_{\gamma\gamma}^2 + \epsilon_{\beta\gamma}^2}$	$\epsilon_{\gamma\alpha}^2 + \epsilon_{\gamma\gamma}^2$	$\epsilon_{\beta\alpha}^2 + \epsilon_{\beta\gamma}^2$	$\epsilon_{\gamma\alpha}^2 + \epsilon_{\gamma\gamma}^2 + \epsilon_{\beta\alpha}^2 + \epsilon_{\beta\gamma}^2$
	$\beta - y$						
3	$\alpha - y$						
	$\gamma - z$	$\frac{\epsilon_{\gamma\beta}^2}{\epsilon_{\gamma\gamma}^2}$		$\frac{\epsilon_{\gamma\beta}^2 + \epsilon_{\alpha\beta}^2}{\epsilon_{\gamma\gamma}^2 + \epsilon_{\alpha\gamma}^2}$	$\epsilon_{\gamma\beta}^2 + \epsilon_{\gamma\gamma}^2$	$\epsilon_{\alpha\beta}^2 + \epsilon_{\alpha\gamma}^2$	$\epsilon_{\gamma\beta}^2 + \epsilon_{\gamma\gamma}^2 + \epsilon_{\alpha\beta}^2 + \epsilon_{\alpha\gamma}^2$
	$\beta - x$						
4	$\alpha - y$						
	$\gamma - x$	$\frac{\epsilon_{\beta\gamma}^2}{\epsilon_{\beta\beta}^2}$		$\frac{\epsilon_{\beta\gamma}^2 + \epsilon_{\alpha\gamma}^2}{\epsilon_{\beta\beta}^2 + \epsilon_{\alpha\beta}^2}$	$\epsilon_{\beta\gamma}^2 + \epsilon_{\beta\beta}^2$	$\epsilon_{\alpha\gamma}^2 + \epsilon_{\alpha\beta}^2$	$\epsilon_{\beta\gamma}^2 + \epsilon_{\beta\beta}^2 + \epsilon_{\alpha\gamma}^2 + \epsilon_{\alpha\beta}^2$
	$\beta - z$						
5	$\alpha - z$						
	$\gamma - y$	$\frac{\epsilon_{\alpha\beta}^2}{\epsilon_{\alpha\alpha}^2}$		$\frac{\epsilon_{\alpha\beta}^2 + \epsilon_{\gamma\beta}^2}{\epsilon_{\alpha\alpha}^2 + \epsilon_{\gamma\alpha}^2}$	$\epsilon_{\alpha\beta}^2 + \epsilon_{\alpha\alpha}^2$	$\epsilon_{\gamma\beta}^2 + \epsilon_{\gamma\alpha}^2$	$\epsilon_{\alpha\beta}^2 + \epsilon_{\alpha\alpha}^2 + \epsilon_{\gamma\beta}^2 + \epsilon_{\gamma\alpha}^2$
	$\beta - x$						
6	$\alpha - z$						
	$\gamma - x$	$\frac{\epsilon_{\alpha\gamma}^2}{\epsilon_{\alpha\alpha}^2}$		$\frac{\epsilon_{\alpha\gamma}^2 + \epsilon_{\beta\gamma}^2}{\epsilon_{\alpha\alpha}^2 + \epsilon_{\beta\alpha}^2}$	$\epsilon_{\alpha\gamma}^2 + \epsilon_{\alpha\alpha}^2$	$\epsilon_{\beta\gamma}^2 + \epsilon_{\beta\alpha}^2$	$\epsilon_{\alpha\gamma}^2 + \epsilon_{\alpha\alpha}^2 + \epsilon_{\beta\gamma}^2 + \epsilon_{\beta\alpha}^2$
	$\beta - y$						

TABLE VI

Nature of the vibration given by the tensor component	Orientation of the crystal	Calculated intensities of components of Raman lines			Observed intensities Line 1050			Observed intensities Line 1361		
		Incident light vector along OZ OY YZ plane			Incident light vector along OZ OY YZ plane			Incident light vector along OZ OY YZ plane		
		S L V along			S L V along			S L V along		
		OZ	OY	YZ	OZ	OY	YZ	OZ	OY	YZ
		S L V along			S L V along			S L V along		
		OZ	OY	YZ	OZ	OY	YZ	OZ	OY	YZ
		OZ	OY	YZ	OZ	OY	YZ	OZ	OY	YZ
		OZ	OY	YZ	OZ	OY	YZ	OZ	OY	YZ
<i>Symmetric</i> $\epsilon_{aa} \neq \epsilon_{\beta\beta} \neq \epsilon_{\gamma\gamma}$ $\epsilon_{a\beta} = \epsilon_{\beta\gamma} = \epsilon_{a\gamma} = 0$ $\epsilon_{aa} = k, \epsilon_{\beta\beta} = l, \epsilon_{\gamma\gamma} = m$	$a-x, \gamma-y, \beta-z$	o	o	o	o	o	o	o	o	o
	$a-y, \gamma-z, \beta-x$	o	o	o	o	o	o	o	o	o
	$a-z, \gamma-y, \beta-x$	o	o	o	o	o	o	o	o	o
<i>Antisymmetric</i> $\epsilon_{\beta\gamma} = n$, the rest being zero	$a-x, \gamma-y, \beta-z$	o	o	o	o	o	o	o	o	o
	$a-y, \gamma-z, \beta-x$	n^2	o	o	o	o	o	o	o	o
	$a-z, \gamma-y, \beta-x$	o	n^2	o	o	o	o	o	o	o
$\epsilon_{a\beta} = p$, the rest being zero	$a-x, \gamma-y, \beta-z$	p^2	o	o	o	o	o	o	o	o
	$a-y, \gamma-z, \beta-x$	o	o	o	o	o	o	o	o	o
	$a-z, \gamma-y, \beta-x$	p^2	o	o	o	o	o	o	o	o
$\epsilon_{a\gamma} = q$, the rest being zero	$a-x, \gamma-y, \beta-z$	o	q^2	o	o	q^2	o	o	q^2	o
	$a-y, \gamma-z, \beta-x$	o	o	q^2	o	o	q^2	o	o	q^2
	$a-z, \gamma-y, \beta-x$	o	o	o	o	o	o	o	o	o

Note—The numerical values of the intensities of lines in this table are not strictly comparative but only serve to show whether the intensities are large or small.

shown in Table V. Cases 1, 3 and 5 alone of this table have been studied in the present case of potassium nitrate. The selection rules for the symmetric and antisymmetric oscillations of the crystal enable us to predict their behaviour for the above-mentioned orientations of the crystal. Accordingly, Table VI shows the expected behaviour of the Raman lines of this crystal for transverse scattering. The observed intensities for the different lines in the spectrum for these orientations of the crystal are also entered in the same table.

The agreement in the intensities of the lines 1050 and 1361 with the theoretically expected values for the symmetrical oscillation is very close, indeed, and consequently we can assign these lines to oscillations of the symmetric type. The discrepancies found in the case of 1050 line in two of these cases may be tentatively attributed to the unavoidable experimental errors such as the effect of convergence of the incident beam and to the slight errors in orientating the crystal due to its finite size. Similar discrepancies have also been found in the cases of sodium nitrate and calcite and hence, no special mechanism need be attributed to these anomalies at present. It is to be noticed, further, that in potassium nitrate we have $\epsilon_{\beta\beta} \approx \epsilon_{\gamma\gamma}$ and is much larger than $\epsilon_{\alpha\alpha}$, so that the intensities of these symmetric oscillations are much less when the incident light vector is along α than along β or γ . That the transverse components of the polarisability tensor are zero for the line 1361 is also evident from the fact that this line practically vanishes in the spectrum recorded with unpolarised incident light when the plane of the NO_3^- ion coincides with the plane containing the incident and scattered beams. The behaviour of the line 1343 almost exactly corresponds to what is expected of an antisymmetric oscillation given by $\epsilon_{\beta\gamma} \neq 0$. It can be also seen from the table that the behaviour of the line 714 corresponds to a combination of a symmetric oscillation with an antisymmetric one given by $\epsilon_{\beta\gamma} \neq 0$. Thus in general, both the degenerate oscillations of the NO_3^- ion actually split up into their components in the crystal with the fundamental difference that in the case of the line 1350 the frequency separation between the split components is much larger than that of the 714 line.

For the low frequency lattice line 82 it is found that the tensors for two separate antisymmetric oscillations describe the behaviour completely. Accordingly it is to be concluded that this line is due to a superposition of two oscillations given by the selection rules $\epsilon_{\alpha\beta}$ alone $\neq 0$ and $\epsilon_{\alpha\gamma}$ alone $\neq 0$. The general behaviour of the line 52 also indicates that it is also due to a superposition of two antisymmetric oscillations given by the selection rules of the same type as for the line 82. However, in this case $\epsilon_{\alpha\beta} < \epsilon_{\alpha\gamma}$ as may

be seen from the observed intensities of this line. Further, the disappearance of this line in Fig 6 *b* is an anomaly for the above assignment and it awaits an explanation.

Analysis of the modes of oscillation of the crystal lattice of potassium nitrate shows (Bhagavantam, 1941) that out of the 18 Raman-active lattice oscillations, 6 are due to rotational oscillations of the NO_3^- ions about the three principal optical directions in the crystal and the rest are due to translational oscillations. The rotational oscillations fall into four classes, A_{1g} , A_{2g} , B_{1g} , and B_{2g} . Among them, those falling under A_{1g} and B_{1g} correspond to oscillations of the NO_3 groups about the normal to their plane (α -axis). The anisotropy in the $\beta\gamma$ plane being extremely small, these oscillations would give rise to only very faint lines. Two of the weak lattice lines observed, namely 100 and 126, might be due to these two oscillations. Their thermal behaviour also supports this assignment. The trigonal symmetry of the crystal above 129°C causes the small anisotropy in the $\beta\gamma$ plane to disappear with the consequent disappearance of these two lines. Rotational oscillations of the NO_3 group about the axes β and γ would, however, give rise to strong Raman lines. It is possible that one of the oscillations about β and one about γ fall together to give the line 82 while the remaining two give rise to the line 52.

In conclusion, the author wishes to record his grateful thanks to Prof. Sir C. V. Raman for his kind advice and assistance during the progress of this investigation.

7 Summary

A careful study of the Raman spectrum of a single crystal of potassium nitrate has yielded the following frequency shifts —52, 82, 100, 126, 143, 714, 1050, 1343 and 1361 cm^{-1} . Out of these, lines 100, 126 and 143 due to the lattice oscillations of the crystal are recorded here for the first time. The most striking observation in a thermal study of the crystal is that these new lattice lines practically disappear in the spectrum of the crystal at a temperature (120°C) just below the transition temperature (129°C .) at which the crystal changes over from orthorhombic to trigonal symmetry. The other lattice lines broaden and shift to lower frequencies with increase of temperature, while the frequency shifts due to the internal oscillations remain appreciably unaltered up to 290°C . However, the split-components 1343 and 1361 of the degenerate oscillation of the NO_3^- ion broaden out and merge into one another even at 170°C . A study of the spectrum of the melt shows that there is no conspicuous change in the frequency shifts due to the internal oscillations due to change of state. A study of the effect of orientation of

the crystal relative to the directions of incidence and observation and different states of polarisation of the incident and scattered radiations shows that the behaviour of the Raman lines in this crystal satisfies the selection rules for the orthorhombic symmetry. The strong birefringence of the crystal causes the internal oscillations to appear more strongly when the incident light vector is in the plane of the NO_3 group than when it is perpendicular to the same. The low frequency lattice lines generally behave in a manner reciprocal to that of the internal oscillations as regards their polarisation characteristics. In the crystal each of the lines 714 and 1350 due to the degenerate oscillations of the NO_3^- ion splits up into a symmetric and an antisymmetric oscillation with the difference that the separation of the split components is much larger for the latter line than for the former.

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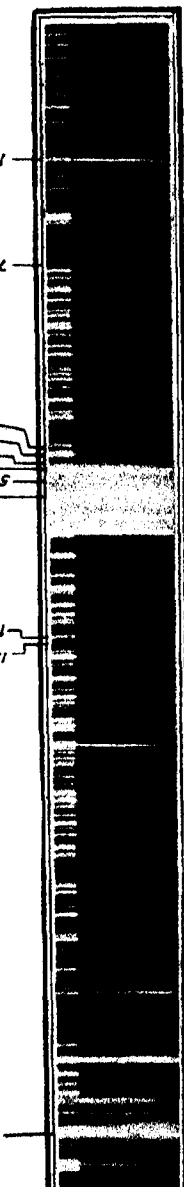


Fig. 1

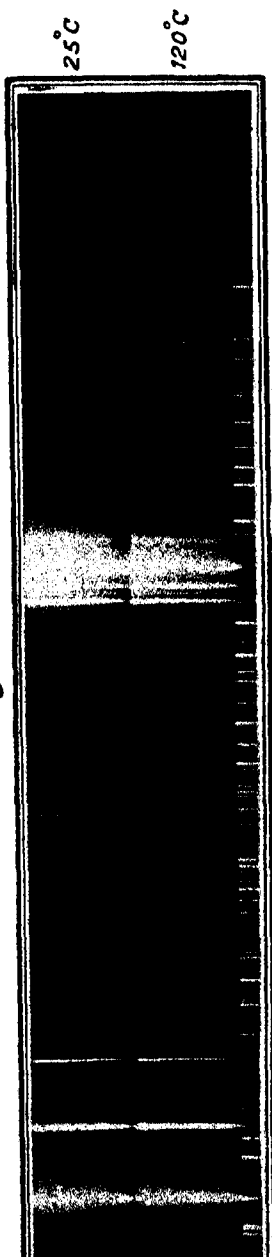
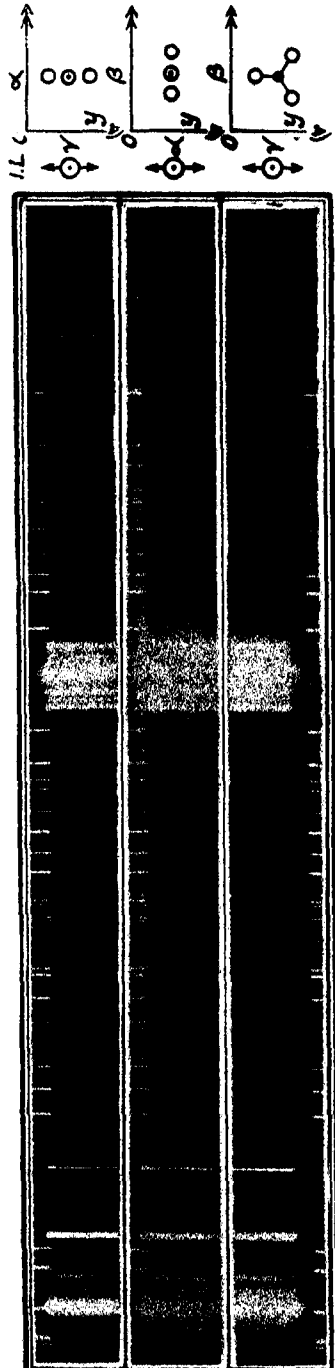


Fig. 2



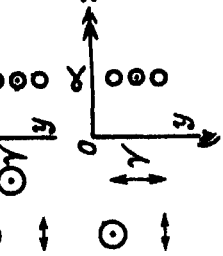


Fig.4

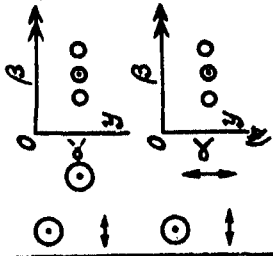
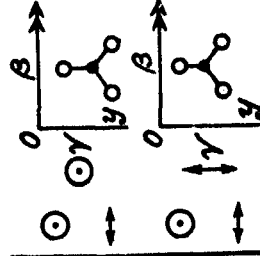


Fig.5



EFFECT OF CRYSTAL ORIENTATION ON THE RAMAN SPECTRUM OF BARYTES

BY T A S BALAKRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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(Communicated by Prof. Sir C V. Raman, Kt, F.R.S., N.L.)

1. Introduction

THE detailed study of light scattering in single crystals has assumed considerable importance in recent times on account of its relation to the theory of the solid state. The study which is conducted both with reference to the orientation of the crystal and the state of polarisation of the incident and scattered light is limited by the difficulty of obtaining a single crystal of suitable size with flawless interior and clear surfaces. In the case of barytes (barium sulphate) the natural crystal answers our purpose very well and can be obtained relatively clear and in large sizes. Barytes naturally crystallises in the di-digonal equatorial class of the orthorhombic system. According to the Dana, the Schoenflies and the Groth systems, it falls under the normal, the holohedral and the rhombic bi-pyramidal classes respectively. This crystal group requires as co-ordinate axes three lines of unequal unit lengths perpendicular to one another. The ratio of the crystallographic axes is given by $a:b:c=0.8152:1.13136$. X-ray studies by James and Wood (1925) show that the atomic structure of barytes possesses a unit orthorhombic cell, the dimensions of which correspond, in terms of the crystal ratio to $2a$, $1b$, $1c$, i.e., $1.6304:1.13136$. From the specific gravity and molecular weight of the crystal, we find the unit parallelepiped contains 4 molecules of BaSO_4 . Of the several forms in which barytes naturally crystallises, though two were available in the collection of Professor Sir C. V. Raman, only crystals having the oblique parallelepiped habit were used in the experiments detailed below.

Despite the abundance and the ease with which crystals of barytes could be secured, it is surprising that very little work has been done on the crystal. It was therefore thought that a detailed study of the scattering in barytes with a view to secure a complete spectrum of the Raman effect would be profitable.

The results that have been obtained and are reported in this paper have justified the investigation

2 Experimental

The investigation was carried out at room temperature (about 25°C) with two crystals of the parallelepiped form. Of the two, the smaller crystal measured nearly $7\text{ cm} \times 6\text{ cm} \times 3\text{ cm}$ and the larger $8\text{ cm} \times 6\text{ cm} \times 4\text{ cm}$. The planes (001), (110) and ($\bar{1}\bar{1}0$) are perfect cleavage planes in the crystal. Hence the crystal was illuminated in a direction perpendicular to the (110) plane, and the light scattered was observed in directions perpendicular to the (001) and (110) planes. The spectrograms obtained are marked (c) and (a) respectively in Fig 1 of the Plate. It was then illuminated along the *c*-axis which is perpendicular to the (001) plane and the scattered light observed perpendicular to the (110) plane, and the spectrogram (b) in the plate was obtained.

The scattering was very weak in the crystal and it was found that exposures extending to over three days were necessary even when the Zeiss three-prism spectrograph with a short camera of focal length 12 cm was used for securing the spectrograms. Of the three orientations, the scattering in the (b) orientation was fainter than in the other two cases which were nearly equal. This necessitated a longer exposure in the (b) orientation in order to obtain a picture of the same density as in the other two spectrograms.

3 Results

Krishnamurti (1930), Nisi (1931) and Rasetti (1931) have worked with single crystals of barium sulphate. The frequency shifts observed by them along with those of the author, obtained in the three orientations, are tabulated in Table I.

Spectrograms obtained by the use of incident unpolarised light for the three different orientations of the crystal described above are reproduced as Fig 1 in the Plate. It is found that no particular orientation gives us the complete Raman spectrum of barium sulphate. A perusal of the table shows that fifteen shifts have been recorded for barium sulphate in all the three orientations put together. Of these the Raman line at 620 wave numbers has not been observed before. The frequency shifts at 614 and 639 wave numbers respectively observed by Nisi but not by Rasetti have been confirmed by the author who has obtained them in two out of the three orientations. But Rasetti reports a line at 631 wave numbers which the author has not obtained in any of the three spectrograms. Similarly, the Raman

TABLE I

Direction of illumination normal to	Frequency shifts in wave numbers per centimetre					
	(110)	(001)	(110)	Krishnamurti	Nisi	Rasetti
Direction of observation normal to	(110)	(110)	(001)			
	452 (5)			} 455	453	451
		458 (5)	458 (5)			462
		614 (4)	614 (4)		614	
	620 (4)					631
		638 (4)	638 (2)		639	
	650 (3)					647
	989 (10)	989 (10)	989 (10)	988	988	989
		1038 (0)				
		1082 (1)				
	1088 (0)		1088 (1)			
	1109 (1)					1105
		1136 (4)			} 1139	
	1142 (2)		1142 (3)			1141
		1158 (2)	1158 (1)			
	1170 (2)					1167

lines at 1038, 1082, 1088, 1136 and 1158 wave numbers respectively have not been observed before. The frequency shift of 1139 wave numbers which Nisi has recorded may be the one at 1136 wave numbers or the one at 1142 wave numbers, both obtained by the author. As against the line at 1109 wave

numbers which has come out in one of the orientations, Rasetti reports one at 1105 wave numbers. Thus six new Raman lines not reported by previous workers have been observed now.

It has been found that the relative intensities of the lines recorded in the spectra vary with the orientation of the crystal. In the orientation marked (b) in Fig 1 of the Plate, the two lines with a frequency shift of 614 and 638 wave numbers have approximately the same intensity. In the other orientation marked (c), the line with the greater frequency shift is less intense. Variations have also been recorded in the relative intensities of the two comparatively intense lines that occur at about 1150 cm^{-1} .

The Raman line occurring at 452 cm^{-1} in one of the orientations and the one at 458 in the other two orientations are not separated in the spectra obtained in the present investigation, whereas Rasetti records two separate lines, in his paper, one at 451 and the other at 462 cm^{-1} . A short focal length camera was used to obtain the spectra, its dispersion was not high which explains the reason for the line appearing as single. But the line at 452 wave numbers is distinct from the one at 458, since a sharp iron line divides these two positions. This can be clearly seen in the Plate.

In addition to the frequency shifts noted by Rasetti and indicated in the table, he also observed some low frequency lines between 50 and 200 cm^{-1} , all of which were faint possessing an intensity of about one-tenth to one-fiftieth of the strongest line at 989 wave numbers. Some of the clear plates obtained by the author show traces of lines in the low frequency region, *i.e.*, up to about 200 cm^{-1} . Unfortunately the spectrograph has a coma extending up to about 100 wave numbers and so precludes the possibility of stating anything definite about the low frequency shifts. This has evidently to be investigated with an instrument more suitable for work in this frequency region.

4. Results with Incident Polarised Light

The behaviour of the Raman lines in the spectrum of barium sulphate was further investigated with the incident light polarised with its electric vector oriented parallel and perpendicular to the plane of observation. Six pictures were taken, two for each of the three orientations of the crystal described above. The intensities of these lines have been estimated visually and recorded by the side of the frequency shifts in Table II.

TABLE II

Showing Intensities and Frequency Shifts of Raman Lines with Incident Polarised Light

Direction of illumination normal to	Frequency shifts in wave numbers per centimetre					
	(110)		(001)		(110)	
Direction of observation normal to	(001)		(110)		(110)	
Orientation of the electric vector with respect to the plane of observation	Parallel	Perpendicular	Perpendicular	Parallel	Perpendicular	Parallel
	(1)	(2)	(3)	(4)	(5)	(6)
	458 (1)	458 (3)	458 (4)	458 (3)	452 (4)	452 (1)
	614 (1)	614 (1)	614 (1)	614 (0)		
	638 (1)		638 (0)		620 (2)	620 (2)
					650 (1)	650 (0)
	989 (2)	989 (10)	989 (10)	989 (2)	989 (10)	989 (2)
	1088 (0)				1095 b (3)	
	1142 (1)	1142 (0)			1142 (0)	1142 (0)
				1145 b (0)		
	1158 (1)				1170 (0)	

5. Discussion

Bhagavantam (1939) has remarked that the degeneracy characteristic of the tetrahedral SO_4 group would disappear in crystals of lower symmetry with the result that the group would have nine distinct frequencies instead of four. A further splitting into 36 modes due to the presence of four SO_4 groups in the lattice cell should occur, but not all of these could be expected to be Raman-active, or to be effectively resolved from each other. As will be seen from Table I, fifteen frequency shifts corresponding to the internal vibrations of the SO_4 group have been recorded in the present investigation with barytes, some of them differing from others only by a few wave numbers.

The selection rules enunciated by Placzek (1934) indicate two important features for the vibration spectra of crystals possessing orthorhombic symmetry. Firstly, of the eight possible vibration classes, four are allowed in

Raman effect and forbidden in the infra-red, three are forbidden in Raman effect but allowed in infra-red and one is forbidden in both. Of the four vibration classes allowed in Raman effect, one is of the symmetric type and three of the anti-symmetric type. If α , β and γ represent the direction of the axes of the ellipsoid of polarisability in orthorhombic crystals, the polarisability tensor has the following six components, $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$, $\epsilon_{\gamma\gamma}$, $\epsilon_{\alpha\beta}$, $\epsilon_{\alpha\gamma}$, $\epsilon_{\beta\gamma}$. In the case of symmetric vibrations, $\epsilon_{\alpha\beta} = \epsilon_{\alpha\gamma} = \epsilon_{\beta\gamma} = 0$, while $\epsilon_{\alpha\alpha} \neq \epsilon_{\beta\beta} \neq \epsilon_{\gamma\gamma} \neq 0$. The three antisymmetric vibration classes are respectively given by only $\epsilon_{\alpha\beta} \neq 0$, only $\epsilon_{\alpha\gamma} \neq 0$, and only $\epsilon_{\beta\gamma} \neq 0$, all the other five tensor components in each case vanishing. The vibrations of the symmetric class give dipole radiation and would therefore be strongly polarised in the normal way. The vibrational modes of the anti-symmetric classes would, on the other hand, give quadrupole radiation and such lines would therefore exhibit anomalous polarisation.

The foregoing indications of theory are in general agreement with the author's results indicated in Table I setting out the experimental results for the cases wherein the incident light is unpolarised and the crystal orientation is varied, and also with those shown in Table II for similar orientations of the crystal, the incident light being polarised. Owing to the fact that the crystal used had the natural faces, two pairs of which were strongly inclined to the axes of the ellipsoid of polarisability, an assignment of all the fifteen observed frequency shifts into the appropriate vibration classes is not possible. It is clear, however, from the data and the photographs that the ν_1 vibrations (989 cm^{-1}) belong to the symmetric class and that the two observed components of the ν_2 frequency (452 and 458 cm^{-1}) should also be assigned to the same class, since both these lines exhibit a normal type of polarisation. This latter result is specially significant in view of the fact that the SO_4 ion in solutions shows the ν_2 frequency as a completely depolarised line. The lines at 1170 and 650 cm^{-1} also are normally polarised and hence may be assigned to the symmetric class. It is noteworthy that they are the components of the higher frequency in the groups ν_3 and ν_4 respectively. The other Raman lines may be assigned to the anti-symmetric class since they exhibit anomalous polarisation. The subject has, however, to be further investigated with a crystal of barytes cut perpendicular to the axes of the ellipsoid of polarisability before a complete analysis of all the frequency shifts is possible.

Matossi and Kindler (1934) in investigating the infra-red spectra of barytes between 2μ and 16μ , observed a very strong band at about 9μ which corresponds to about 1100 wave numbers per centimetre. The author has recorded three Raman lines with shifts of about 1082 , 1088 and 1109 cm^{-1}

respectively lying in this frequency region. The line at 1082 cm^{-1} has appeared in one of the orientations, 1088 cm^{-1} in the other and both 1088 and 1109 cm^{-1} in the third orientation. Similarly a Raman line with a shift of 638 cm^{-1} has come out in two orientations and another line at 650 cm^{-1} in the third orientation, in the vicinity of the very strong infra-red band reported at 15.65μ (640 cm^{-1}). It should however be emphasised that the approximate correspondence noted above cannot be regarded as an identity in as much as the selection rules of Placzek demand that Raman-active oscillations should be forbidden in the infra-red and *vice versa*. No trace was found in the spectrum of the scattered light corresponding to the two weak bands at 12.35μ (810 cm^{-1}) and 10.81μ (925 cm^{-1}) in the infra-red.

Schæfer and Schubert (1916) by using two slices of barytes cut parallel to the plane containing the *a*- and *b*-axes and the *a*- and *c*-axes (the axes are given here in the crystallographic notation) have investigated the infra-red reflection maxima with radiation polarised parallel to all the three axes. With the electric vector parallel to the *a*- and *c*-axes, they obtain maxima at 8.30μ (1204 cm^{-1}) and 8.93μ (1120 cm^{-1}) respectively. On the other hand no reflection maximum is detectable with the electric vector parallel to the *b*-axis. It may be remarked that no Raman line has been observed corresponding to the 8.30μ band in any of the spectrograms of the author. As regards the band at 8.93μ , according to Schæfer and Schubert, the oscillation should appear when the electric vector is parallel to the *c*-axis and vanish altogether when it is perpendicular. The Raman line at about 1142 cm^{-1} , however, behaves quite differently and has been recorded in all the six spectrograms except one where it is probable that the line has not appeared because of the extreme weakness of scattering in that setting.

The author wishes to record his grateful thanks to Prof. Sir C. V. Raman, F.R.S., for his kind interest in the work.

6 Summary

The Raman spectrum of single crystals of barytes has been studied for three different orientations. It is found that the frequency ν_2 of the sulphate ion splits into two lines at 452 cm^{-1} and 458 cm^{-1} . The ν_3 frequency occurs as four lines at 614 , 620 , 638 and 650 cm^{-1} . The ν_1 frequency, which is the symmetric oscillation of the ion, remains single at 989 cm^{-1} . The ν_4 frequency splits into as many as eight components at 1038 , 1082 , 1088 , 1109 , 1136 , 1142 , 1158 and 1170 cm^{-1} . None of the three orientations of the crystal gives the complete Raman spectrum, some of the components vanishing in particular orientations, while the intensities of the others vary. The

apparent disagreements in the results of the previous workers are thus explained. These changes have been observed using only incident unpolarised light. The Raman spectra have also been investigated with incident light polarised in and perpendicular to the plane of observation. The polarisation studies indicate that the frequencies at 452, 458, 650, 989 and 1170 should be assigned to the symmetric and the other lines to the anti-symmetric class of vibrations

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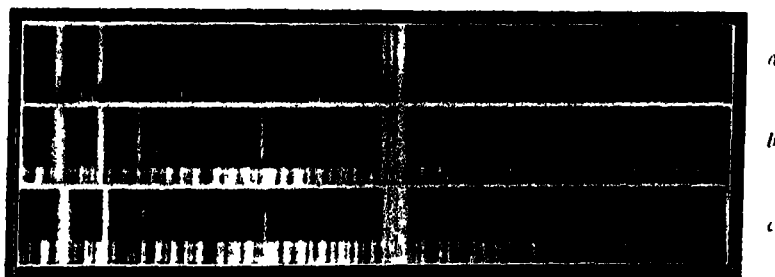


FIG. 1 Raman Spectra of Barium Sulphate in different Orientations

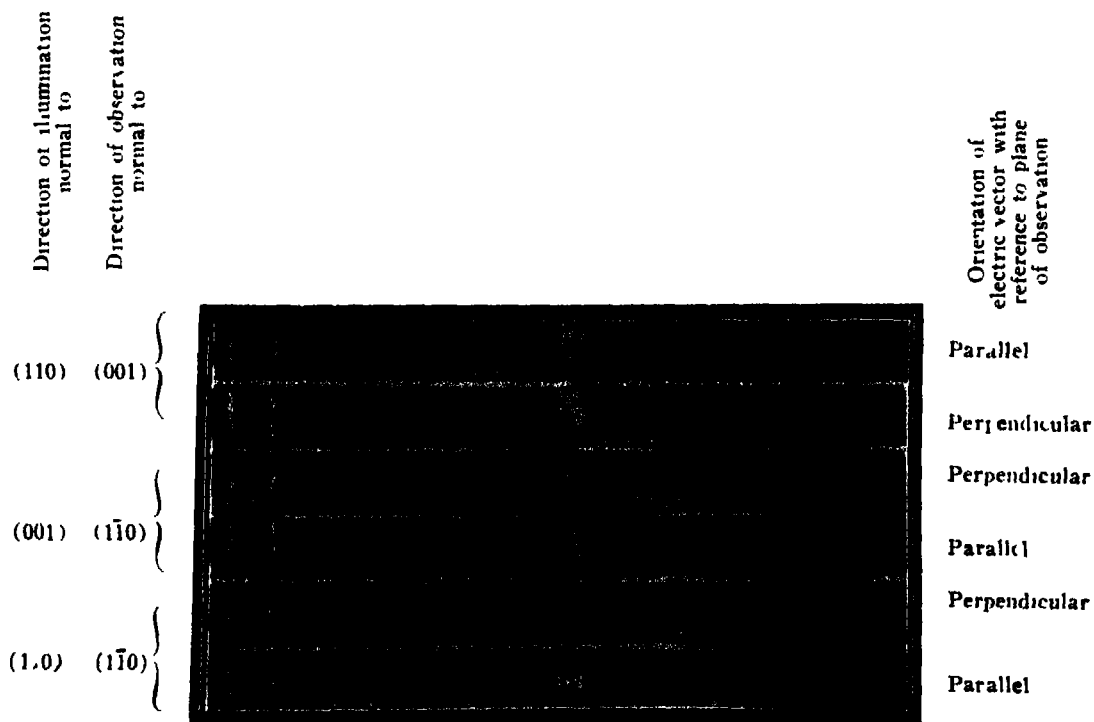


FIG. 2. Raman Spectra of Barium Sulphate with incident polarised light

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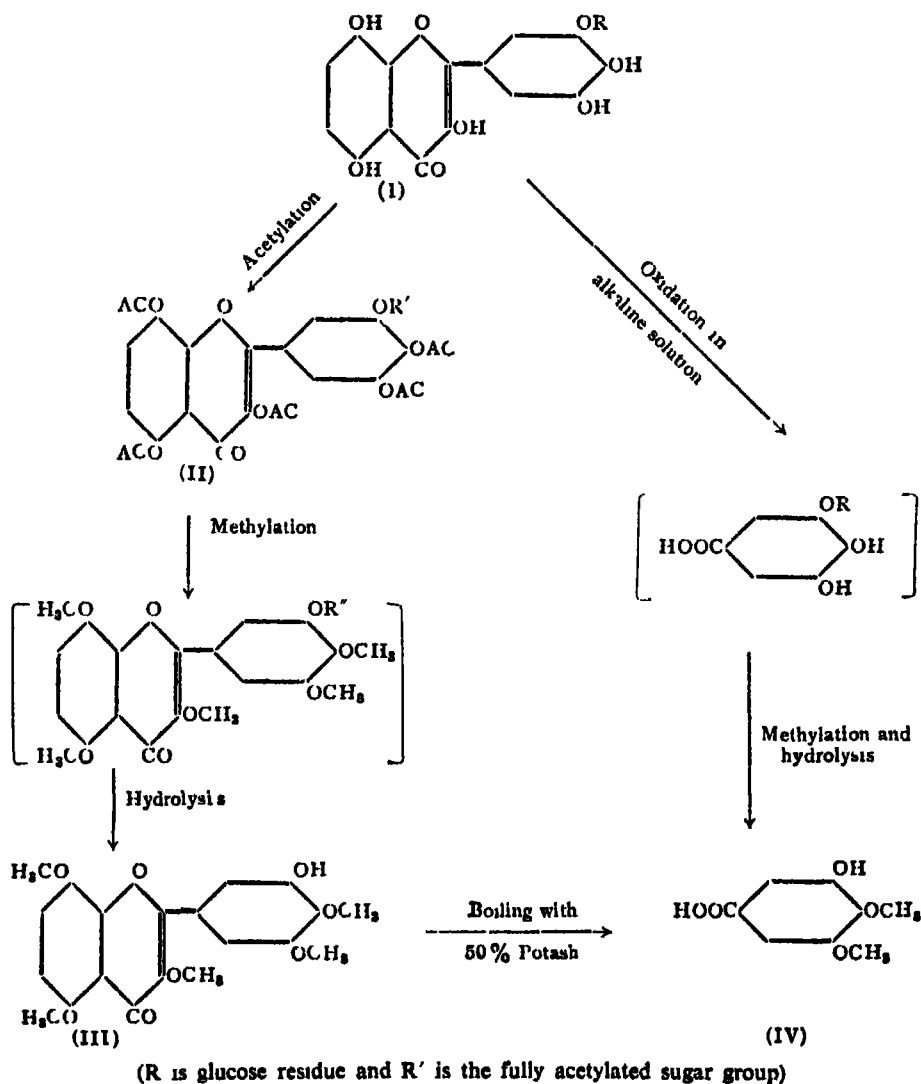
BY P. SURYAPRAKASA RAO AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University, Waltair)

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It has recently been shown that the colouring matter of the flowers of *Hibiscus cannabinus* consists of a new flavonol called cannabiscetin and its glucoside, cannabiscitrin, the latter being the main component. From a study of its reactions and the degradation products, the constitution of the flavonol has been deduced to be 3:5:8:3':4':5'-hexahydroxyflavone.¹ Cannabiscitrin is concluded to be a monoglucoside from the combustion analysis and from the yields of the products of hydrolysis. In giving an orange-red precipitate with lead acetate and in being hydrolysed with difficulty by acids, the new glucoside ($C_{21}H_{20}O_{13}$) resembles gossypitrin, herbacitrin and quercimeritrin which carry the sugar groups in position 7, and this behaviour shows that it is not a 3-glucoside. Neither the 5- nor the 8-hydroxyl group seems to be involved in the glucoside-formation, since the substance undergoes ready oxidation to give the "gossypetone" reaction. It may, therefore, be concluded that the sugar group is present not in the benzopyrone ring but in the side phenyl nucleus. This surmise has been substantiated and the exact position involved determined in the following manner: Cannabiscitrin is completely methylated through the acetyl derivative² (II) and the product hydrolysed in order to remove the sugar part. When the resulting pentamethyl cannabiscetin is decomposed with boiling 50% potash, a dimethyl gallic acid is obtained. This is different from syringic acid, and found to be identical with 4:5-dimethyl gallic acid (IV). The same compound is also obtained by subjecting the glucoside to aerial oxidation in cold alkali, directly methylating the products and finally effecting the removal of the sugar molecule by acid hydrolysis. Cannabiscitrin is, therefore, concluded to be the 3'-glucoside (I), and the pentamethyl-ether mentioned above to be 3:5:8:4':5'-pentamethyl cannabiscetin (III). The changes involved are represented diagrammatically below.

Thus cannabiscitrin is unusual amongst glycosides of flavones and flavanols in holding the glucose residue in the side phenyl nucleus. The cases so far known belonged to only two categories (1) the 3-glycosides and (2) the 7-glycosides. Recently it has been reported by us³ that in butrin the flavanone structure carries one of the glucose units in the 3'-position, and



hence this type of glycosides seems to be more common than originally thought of

Experimental

Hydrolysis of Cannabiscitrin Estimation of the Aglucone and the Glucose.—

The glucoside (2 g) was hydrolysed by boiling with 7% sulphuric acid (100 c c). After heating for a few minutes the solid went into solution, and after twenty minutes the aglucone began to separate out, giving rise to bumping. The heating was, therefore, continued on a boiling water-bath

for an hour and a half more. The contents were cooled and filtered. The filtrate was almost colourless and did not yield any appreciable amount of the aglucone on ether extraction. So the residue after the filtration was dried in air, and weighed accurately. The acid filtrate which contained the glucose was made slightly alkaline by the addition of the requisite amount of sodium hydroxide, made up to a known volume, and the sugar estimated by titration against standard Fehling solution.

The amounts of the aglucone and the glucose produced as a result of the hydrolysis of the glucoside were calculated. [Found Aglucone, 63.4, Glucose, 33.6, $C_{21}H_{20}O_{13}$, 3 H_2O requires Aglucone ($C_{15}H_{10}O_8$, H_2O), 62.9, Glucose, 33.7%]

Gossypetone Reaction with the Glucoside — The substance (0.5 g) was dissolved in absolute alcohol (30 c.c.) and *p*-benzoquinone (0.2 g) in the same solvent (2 c.c.) was added. The original solutions were both yellow in colour, and the mixture immediately assumed a dark red colour, and a dull red solid began to separate out gradually. The next day it was filtered and washed with a small quantity of absolute alcohol. It was maroon-coloured, looking like red phosphorus, and did not melt below 300° . When treated with a drop of dilute potassium hydroxide, it dissolved producing a blue solution, which became red on acidification. When the substance was suspended in water and reduced with sulphur dioxide, the original glucoside was regenerated.

Methylation of the Glucoside and Subsequent Hydrolysis *Isolation of 3.5.8:4'-5'-Pentamethyl Cannabiscitrin* — Cannabiscitrin acetate (1 g) was dissolved in acetone (40 c.c.) and dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.) were added to the solution alternately in small quantities. The mixture was shaken vigorously after each addition, when it assumed a lemon yellow colour which faded gradually. Thereupon further quantities of dimethyl sulphate (5 c.c.) and the sodium hydroxide (5 c.c.) were added and finally the medium was made definitely alkaline by the gradual addition of 10 c.c. more of the above alkali. There was a gradual development of heat throughout the process, and during the later stages the mixture became so hot that there was actual boiling. After leaving overnight, it was gently boiled under reflux on a water-bath for an hour. Then almost all the solvent was driven off, the alkaline solution was just neutralised, and then sufficient amount of concentrated sulphuric acid was added so as to render the solution 7% acid. It was finally boiled under reflux for 2 hours. As no solid separated out on cooling, the contents were repeatedly extracted with ether. On evaporating off the solvent, the ether extract yielded an

almost colourless substance When crystallised from dilute alcohol using a little animal charcoal, it was obtained as narrow rectangular plates in fern-like structures, melting at $191-92^{\circ}$ [Found in the sample dried at 120° in *vacuo* OCH_3 , 39.7, $\text{C}_{18}\text{H}_{14}\text{O}_2$ (OH) $(\text{OCH}_3)_2$ requires OCH_3 , 40.0%]

Alkaline Oxidation of the Pentamethyl Ether. Isolation of 4,5-Dimethyl Gallic Acid—The pentamethyl cannabiscetin (0.5 g) was boiled under reflux in a silver flask with 50% potash (20 c.c.) for 6 hours. After cooling, the alkaline solution was diluted, filtered and the clear filtrate acidified with hydrochloric acid. On extraction with ether, the solution yielded a small amount of a crystalline solid which was, however, brown in colour. It was purified by dissolution in sodium bicarbonate and subsequent reprecipitation. On crystallisation from dilute alcohol, the acid was obtained as narrow rectangular plates melting at $193-95^{\circ}$. It was easily soluble in hot water, and the solution did not develop any characteristic colour, when treated with a drop of ferric chloride. The substance was found to be a dimethyl ether of gallic acid [Found OCH_3 , 31.0, C_6H_2 (OH) $(\text{OCH}_3)_2$ COOH requires OCH_3 , 31.3%]. It was not, however, identical with syringic acid (m.p. $204-05^{\circ}$) since the mixed melting point of the two substances was depressed and indefinite, ranging from $155-75^{\circ}$. All the properties indicated that the acid should be 4,5-dimethyl gallic acid, and this was confirmed by taking the mixed melting point of the two substances, it was undepressed. For this purpose an authentic sample of 4,5-dimethyl gallic acid was prepared from vanillin according to the method of Shriner and McCutchen.⁴ Vanillin was treated with bromine in glacial acetic acid solution, when 3-bromovanillin was produced. It was then methylated with dimethyl sulphate and alkali to yield 3-bromo-4,5-dimethoxy benzaldehyde, which was subsequently oxidised with alkaline potassium permanganate to form the corresponding acid. The bromine atom in this acid was finally replaced by a hydroxyl group by heating it in a sealed tube with dilute alkali and copper powder. 4,5-Dimethyl gallic acid thus obtained melted at $193-95^{\circ}$ and not at $184-85^{\circ}$ as stated by Shriner and McCutchen (*loc. cit.*) [Found: OCH_3 , 31.2; C_6H_2 (OH) $(\text{OCH}_3)_2$ COOH requires OCH_3 , 31.3%]

Further Methylation of the Pentamethyl Ether. Preparation of Hexamethyl Cannabiscetin—The pentamethyl cannabiscetin obtained above was dissolved in excess of 20% alkali and methylated with dimethyl sulphate in the usual manner. After the completion of the reaction, the product was acidified with dilute hydrochloric acid, and then extracted with ether. On evaporating off the solvent, a pale yellow solid was obtained. It was purified

by crystallisation from alcohol using a little animal charcoal. The substance was found to be identical with hexamethyl cannabiscetin melting at 174–75°

Oxidation of Cannabiscitrin Isolation of 4, 5-Dimethyl Gallic Acid—The glucoside (1 g) was dissolved in 50% potash (15 c.c.) and the blood red solution formed was frequently shaken and exposed to air for 24 hours. It was then diluted to about 40 c.c. and shaken with excess of dimethyl sulphate (15 c.c.) in small quantities. After leaving overnight, the mixture was heated on a water-bath for about half an hour to destroy the excess of dimethyl sulphate. The solution was still alkaline. It was therefore just neutralised with hydrochloric acid, and then the calculated amount of concentrated sulphuric acid was added so as to render the solution 7% in its acid content. It was then boiled under reflux for 2 hours, and when cooled a small amount of resin separated out. This was removed by filtration using a fluted filter, and the clear filtrate was then extracted with ether. On distilling off the ether, a brown viscous liquid was left behind. When it was left overnight in the frigidaire, an almost colourless crystalline solid separated out. It was filtered and recrystallised from boiling water using a little animal charcoal, when it appeared as colourless needles and plates melting at 192–94°. The acid was found to be identical with 4, 5-dimethyl gallic acid.

Summary

The final constitution of cannabiscitrin has been established. It is a monoglucoside of the flavonol cannabiscetin, carrying the sugar group in the side phenyl nucleus in the 3'-position. This has been arrived at from the following considerations—It gives the gossypetone reaction and after complete methylation and hydrolysis, it yields a pentamethyl cannabiscetin which on decomposition produces 4, 5-dimethyl gallic acid. The same acid is also obtained by first decomposing cannabiscitrin with alkali, and then subjecting the products to methylation and subsequent hydrolysis. Thus the glucoside belongs to an unusual type and resembles butrin.

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KINETIC STUDIES IN ESTER HYDROLYSIS

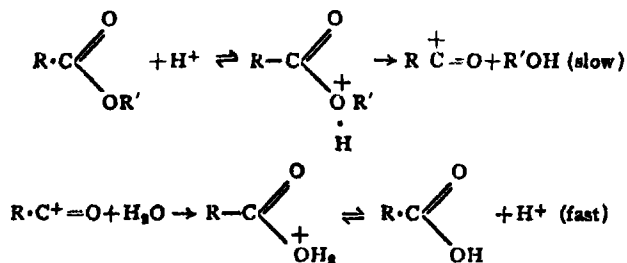
Part I. The Hydrolysis of Halogeno-aliphatic Esters

BY S V. ANANTAKRISHNAN AND S KRISHNAMURTI

(From the Annamalai University Chemical Laboratories, Annamalai-nagar)

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THOUGH the hydrolysis of esters has been the subject of study for nearly half a century since de Hemptinne's first paper,⁷ it is only recently that a systematic study has been made. The accepted mechanism for both acid and alkaline hydrolysis is that due to Lowry¹³ involving a common intermediate complex. For acid hydrolysis, three alternative courses are possible, but, by the use of isotopic oxygen, Ingold, Day and Datta³ have shown that the best scheme is as follows:—



With the advent of the electronic theory, it is natural to use it in the interpretation of group influences on hydrolytic reactions as well. The susceptibility to polar influences has been well demonstrated by Kindler working with benzoic esters¹² and the more systematic and thorough studies of Ingold and Nathan,¹⁰ Evans, Gordon and Watson⁵ and Hinshelwood and co-workers.⁹ It has further been noticed that in the case of meta and para substituents, the PZ values of the Arrhenius' equation remains the same while E changes with structure. Now, the activation energy may be considered to involve a repulsion term and a bond energy term in which the latter is influenced by the polar characteristics of the substituent group. Evans and Jenkins⁶ were able to obtain for the hydrolysis of benzoic esters a relation of the form

$$E = E_b + E_x/\epsilon_{30}$$

where E is the activation energy, E_b the bond energy and E_x/ϵ_{30} is the repulsion energy.

Most of the work generally described deals with aromatic esters while the aliphatic series seems to be comparatively neglected. It is well known that the behaviour of halogens is anomalous in the aromatic series among themselves, though they fall in the right position as regards the group as a whole. Further, it is usual to assume, since saturated carbon atoms are involved, that the influence of the halogens arises only from the transmission of the inductive effect. The present communication deals with a preliminary investigation of a few halogeno-aliphatic esters, a systematic study of which may be expected to clarify the position.

The choice of Dioxan-water as solvent needs some explanation. Usually the reaction has been studied in alcohol-water and acetone-water systems. The range of working temperature available precluded the use of acetone for any fair degree of accuracy and at the same time it was considered desirable to avoid a solvent taking part in the reverse reaction. At the same time, for comparison of results, a solvent of about the same dielectric constant and viscosity had to be chosen. The influence of the solvent is considered in greater detail in the next part. All the reactions described herein have been carried out in 60% dioxan (by weight) and the results are tabulated below (Tables I, II, III and IV).

TABLE I
Ethyl Esters of Alkyl-substituted Acids

Acid	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^5$	E (from graph)	PZ
		5	10	20	40			
Acetic	35	69	138	285	636	13.09	16,930	1.47
	42	37	75	150	342	24.41		
	50	22	42	84	178	43.01		
	60	9	18	36	75	100.2		
Propionic	35	78	162.5	345	780	10.63	15,960	0.24
	42	45	87.5	187.5	425	19.93		
	50	25	50	102.5	220	36.13		
	60	12.5	25	51	110	68.75		
<i>n</i> -Butyric	35	190	380	740	1600	4.93	15,510	0.065
	42	85	175	365	830	10.03		
	50	45	95	190	380	19.36		
	60	20	40	90	200	41.69		

TABLE II
Ethyl Esters of Chloro Acids

Acid	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^3$	E (from graph)	PZ
		5	10	20	40			
Chloroacetic	35	102	202	420	864	8 686	16,640	0 61
	42	60	120	240	522	15 05		
	50	24	54	121	263	31 51		
	60	12	24	54	128	75 27		
α -Chloropropionic	35	234	468	1044	2502	3 763	15,060	0 20
	42	108	244	522	1170	7 169		
	50	80	162	288	630	12 04		
	60	43	72	145	324	25 09		
β -Chloropropionic	35	300	660	1590	4380	2 441	16,070	0 065
	42	180	360	900	2460	4 516		
	50	108	225	480	1200	7 785		
	60	50	100	210	570	17 37		

TABLE III
Ethyl Esters of Bromo Acids

Acid	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^3$	E (from graph)	PZ
		5	10	20	40			
Bromoacetic	35	72	165	378	888	10 39	15,780	0 16
	42	48	105	240	571	15 85		
	50	27	54	114	270	32 26		
	60	12	24	54	126	69 49		
α -Bromopropionic	35	390	825	1800	4260	2 030	16,830	0 20
	42	240	465	945	2040	3 844		
	50	90	225	480	1050	7 749		
	60	60	114	225	504	16 43		
β -Bromopropionic	35	390	900	2280	5400	1 737	18,690	3 40
	42	210	510	1140	2640	3 346		
	50	90	210	540	1320	8 370		
	60	48	100	225	570	17 37		

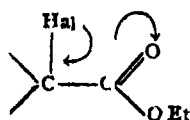
TABLE IV
Ethyl Esters of Iodo Acids

Acid	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^5$	E (from graph)	PZ
		5	10	20	40			
Iodoacetic	35	180	350	654		5.408		
	42	102	243	483	960	7.460	14,230	0.007
	50	57	120	246	510	14.80		
	60	24	57	111	228	32.26		
α -Iodopropionic	35	1230	2280	4560	10,080	0.8065		
	42	480	1020	2070	4230	1.135	17,260	0.16
	50	300	600	1200	2490	3.011		
	60	120	276	510	1020	6.949		
β -Iodopropionic	35	510	990	2250	5310	1.69		
	42	300	690	1290	2850	2.779	16,320	0.068
	50	150	315	645	1380	5.645		
	60	75	156	303	630	11.89		

It will be noticed that the alkyl substituents do not affect the magnitude of the rate constant to any considerable degree but the drop in the value from ethylpropionate to ethyl butyrate is pronounced, while that from ethylacetate to propionate is slight. This change is traceable to two factors: first, the influence of the group on the formation of the transition state complex and secondly the steric factor. Alkyl groups (class + I) facilitate polarisation of the C=O bond, thereby stabilizing the complex. Further it is known from other studies that the ethyl group is a better electron-donor than the methyl. Consequently, there is a slowing down in the reaction as one ascends the homologous series, the rate tending to a more or less constant value higher up the series. This increase in stability of the activated complex is combined with a corresponding ease of formation of the complex as well. A diminishing energy of activation from ethyl acetate to ethylpropionate bears out this conclusion. The value of E also presumably tends to a constant value in line with other properties of the aliphatic acids (*e.g.*, ionisation constant) which are influenced by polar characteristics of substituents.

The influence of the halogens is of a more complex nature. Such halogen derivatives belong to the class - I + T, the inductive and tautomeric

effects varying with the halogen. As is well known, the $-I$ effect is in the order $Cl < Br < I$. One may therefore expect that reactivity towards electrophilic reagents will diminish as one changes from the chloro to the iodo-compound. The trend in the rate constant for ester hydrolysis (*vide* Tables II, III and IV) clearly brings this out. The behaviour of ethyl bromoacetate at lower temperatures is somewhat anomalous. The slowest reaction among esters studied is the hydrolysis of ethyl α -iodopropionate. Now, Pauling and others have shown that the C-halogen bond possesses a certain amount of double bonded character¹⁴ arising from resonance and this gives rise to a "conjugated system" in the α -halogeno esters



The iodine atom is the most polarisable and one may expect from *a priori* considerations that this resonance effect will be most pronounced in α -iodopropionic ester

Taking the halogens as a whole, the $-I$ effect diminishes the ease of formation of the activated complex while the $+T$ acts in the opposite direction. The resultant of these two opposing tendencies must account for the observed values of activation energy and rate constant. In the case of the halogeno acetates the value of E progressively decreases from the chloro to the iodo-derivative (the mono-halogeno compounds alone are considered here). On the other hand, in the case of α -halogeno propionates the position is reversed. α -Chloropropionate exhibits the lowest energy of activation while the iodo-compound shows the highest. One has to take into account, not merely, the halogen but also the alkyl group, with the result that group influences are more complex. Probably, the electron donating alkyl group attached to the same carbon atom as the halogen suppresses wholly or in part the $+T$ effect. The net result is a decrease in the ease of formation and the stability of the transition state, a slowing down of the reaction as a whole and a reversal of the relative order of the halogens. Ethyl iodopropionate is found to give the highest value for E .

The β -halogenopropionates are of a different type. An intervening saturated carbon atom, which might considerably diminish even the inductive effect, makes the influence of the tautomeric effect on the carbethoxy group negligible. The CH_2Hal group appears essentially as an electron acceptor and the reaction becomes slow. The trend of E values shows a slight increase from the chloro to the iodo-compound.

Our attention so far has been directed to the relation between one of the Arrhenius parameters, E , and the substituent. It is now necessary to consider the other parameter. Plotting $\log_{10} k$ against E (Fig 1) it will be noticed

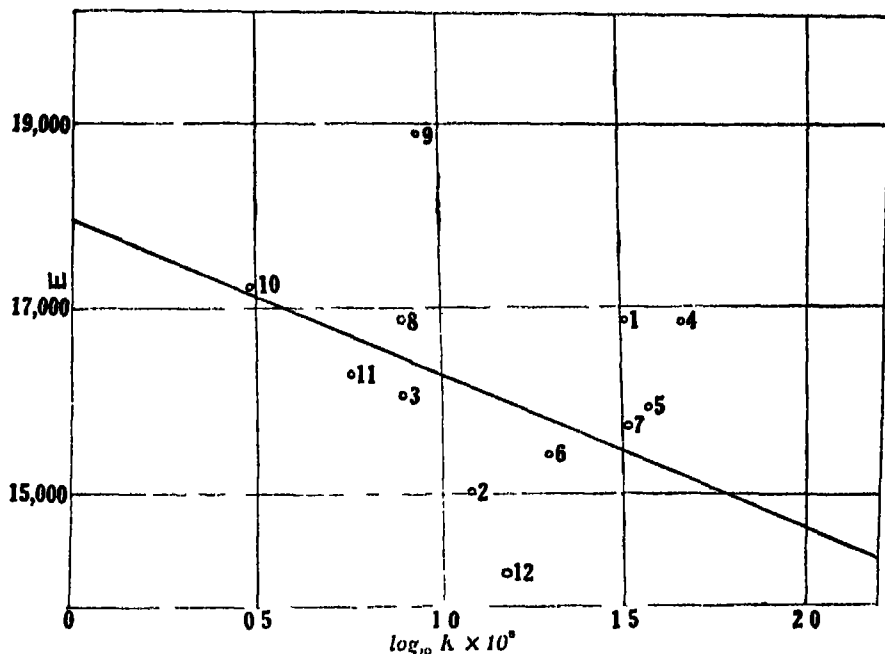


FIG 1

KEY TO NUMBERS

- | | |
|-----------------------------------|-----------------------------------|
| 1 Ethyl acetate | 7 Ethyl bromacetate |
| 2 Ethyl propionate | 8 Ethyl α bromopropionate |
| 3 Ethyl butyrate | 9 Ethyl β bromopropionate |
| 4 Ethyl chloracetate | 10 Ethyl iodopropionate |
| 5 Ethyl α chloropropionate | 11 Ethyl α -iodopropionate |
| 6 Ethyl β chloropropionate | 12 Ethyl β iodopropionate |

that very few points lie along the slope — $2.303 RT$. Most of the points are distributed at random. This is a clear indication that the aliphatic esters studied differ on this important aspect from the aromatic compounds. The PZ values are obviously different. Now, this factor is primarily dependent on the mean molecular diameter of the interacting molecules and on the orientation of the molecule. While an increase in size increases the frequency of molecular collisions, in the present instances, this very factor appears to lead to ineffective collisions not involving the carbethoxy group. Consequently, the iodo-compound has the smallest value for this probability factor.

This same result can also be shown in another way Hinshelwood⁶ has shown that if the constant χ in the equation

$$k = \chi e^{-E/RT}$$

were the same for all reactions, there is a linear relationship between the energy of activation and the temperature at which the reaction attains a given rate. An examination of the present series gives a random distribution of points when the E vs T curve is plotted for a speed such that the reaction is half completed in one hour using the concentrations used (Table V and Fig. 2).

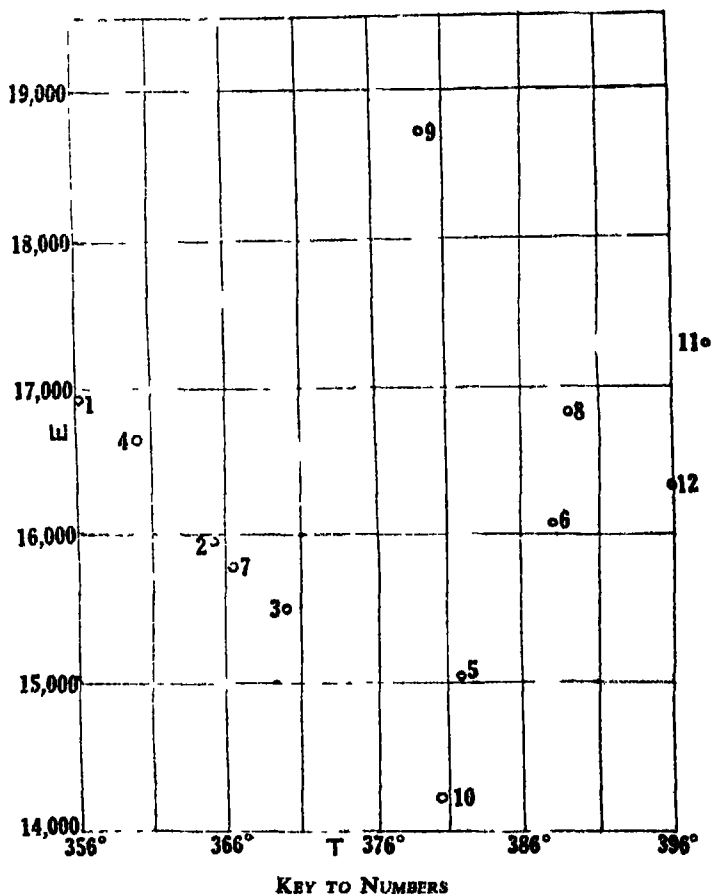


FIG. 2

E—Energy of activation in calories

T—Temperature in degrees absolute for equal velocity of reaction

TABLE V

Hydrolysis of ethyl ester of acid	Temperature of equal velocity in ° absolute	Energy of activation
Acetic	355.8	16,930
Propionic	364.9	15,960
<i>n</i> -Butyric	369.0	15,510
Chloroacetic	360.0	16,640
α -Chloropropionic	381.7	15,060
β -Chloropropionic	387.9	16,070
Bromoacetic	366.5	15,780
α -Bromopropionic	387.9	16,830
β -Bromopropionic	379.5	18,690
Iodoacetic	380.0	14,230
α -Iodopropionic	398.0	17,260
β -Iodopropionic	396.0	16,320

Any quantitative deductions on this aspect may be attempted only after a further study of a larger number of substituted aliphatic esters

Experimental

Dioxan (Kodak) was purified by the method of Eigenberger⁴ and the fraction, b p, 104° C and m p 11.8° C, was used. Exactly decinormal solutions of hydrochloric acid were prepared using purified dioxan diluted with 40% by weight of water.

Ethyl esters of acetic, propionic, *n*-butyric, monochloroacetic, monobromoacetic, α -bromopropionic and β -iodopropionic acids (Kahlbaum) were used, after purification by the usual processes, fresh samples being used for each set of experiments. Ethyl- β -chloropropionate was of Schucardt's manufacture.

Ethyliodoacetate was prepared by a modification of Kekule's method.¹¹ 35 Grams of ethylchloroacetate was refluxed with 50 grams of sodium iodide (molar proportions) in dry acetone solution for 3 hours. After filtering off the sodium chloride, the solvent was distilled off. From the residue, the fraction boiling between 178° and 180° was taken, washed with sodium carbonate and water, dried over anhydrous sodium sulphate and fractionated. Yield 40 g pure ester b p. 179–80°.

Ethyl- α -chloropropionate was prepared by the method of Walker.¹⁵ Care is needed in controlling the initial violent reaction of lactic acid with phosphorous pentachloride, but warming is needed in the later stages to complete the reaction. The pure ester boiled at 47°/20 mm.

Ethyl- α -iodopropionate was obtained by the method of Bodroux and Taboury,¹ b p 78° 5/28 mm.

Ethyl- β -bromopropionate was prepared by the method described in *Organic Syntheses*,² b p 65°/15 mm.

The reactions were carried out in an electrical thermostat between 35 and 60° C, the accuracy of control being ± 0.02 . Air-tight, glass stoppered bottles of resistance glass were used as containers for the reaction mixture, 200 c.c. of the acid solvent was allowed to attain the temperature of the thermostat, calculated amounts of the ester for a decimolar solution added and the change with time measured acidimetrically. N/40 Baryta was used for the estimations involving unsubstituted compounds and ammonia of the same strength for the halogenated esters. The catalytic action of the acid products of hydrolysis was negligible (see also Hinshelwood *et al.*). The loss of esters by volatilisation was also inappreciable.

Summary

The kinetics of acid hydrolysis of some aliphatic esters have been studied at four different temperatures in 60% dioxan. The effect of the halogen on the parameters of the Arrhenius equation have been discussed from the standpoint of the electronic theory of organic reactions.

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KINETIC STUDIES IN ESTER HYDROLYSIS

Part II. The Influence of Solvent on the Reaction

BY S V ANANTAKRISHNAN AND S KRISHNAMURTI

(From the Annamalai University Chemical Laboratories, Annamalainagar)

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THOUGH correlation between reaction in the gas phase and reactions in solution has been noticed, it is fairly established that a solvent exerts considerable influence on the course of reactions. A solvent may be termed "inert" if it is unassociated, nonpolar and chemically "saturated" and there is no difference in the rate of a reaction whether in gaseous phase or in solution. Such solvents are, however, of very limited application and are unsuitable for reactions of the type under investigation. Qualitative relationship has been established between the velocity constant of bimolecular reactions and the dielectric constant, cohesion and viscosity of the solvent^{4,7}. Using solvents of "similar type", Evans and Jenkins¹ obtain for the alkaline hydrolysis of benzoic esters the relation

$$E = E_B + E_X/\epsilon_{20},$$

where E_B is the bond energy, $E_X/\epsilon_{20} = E_R$ the repulsion energy and ϵ the dielectric constant of the medium. The extent of solvent influence will naturally depend on the ratio E_R/E and will be small if the ratio is too small a fraction. The solvent effect has also been thoroughly studied only in a few cases.

Now, molecules in general may exert influences on one another and, when within molecular distances from one another, there must be a pronounced change in the potential energy curves. This effect must be especially noticeable in solution. Consequently the first effect that might be observed is a difference in the energy of activation. It is also noticed that where E changes with solvent, PZ of the reaction velocity equation changes concurrently.

In Part I, the influence of substituent on the parameters of the Arrhenius equation has been considered and in the present communication attention is directed to solvent influences. Since it was considered desirable to alter both viscosity and dielectric constant, glycerol was chosen as the medium, varying amounts of water being added to alter both these physical properties.

The choice of this solvent, however, imposed a severe restriction on the choice of esters on account of their low solubility in glycerol-water systems but this does not affect the validity of the conclusions arrived at

Three esters have been studied in four different concentrations of glycerol and at four different temperatures. For comparison, the relevant results of Part I in 60% dioxan and values calculated from the data of Hinshelwood² for 60% alcohol are also included. The results are summarised in Tables I-VII.

TABLE I
Hydrolysis of Ethyl Acetate

Medium	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^4$
		5	10	20	40	
20% Glycerol	35	33.0	70.0	141.0	319.0	25.57
	42	20.0	39.0	78.0	177.0	47.54
	50	10.0	20.0	40.0	87.0	90.33
	60	4.5	9.5	19.0	42.0	190.1
40% Glycerol	35	30.0	61.0	125.0	290.0	29.45
	42	15.0	31.0	67.0	160.0	56.45
	50	9.5	19.25	37.5	88.0	96.79
	60	3.5	7.75	16.5	39.75	235.7
60% Glycerol	35	25.0	54.0	115.0	288.0	32.26
	42	11.0	28.0	63.0	169.0	60.22
	50	7.0	16.0	35.0	95.0	108.4
	60	3.5	8.0	18.0	47.0	208.4
80% Glycerol	35	34.0	69.0	146.0	.	25.81
	42	18.0	38.0	80.0		47.26
	50	9.0	19.0	40.0		93.46
	60	5.0	8.0	20.0		193.6

TABLE II
Hydrolysis of Ethyl Propionate

Medium	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^5$
		5	10	20	40	
20% Glycerol	35	38 0	72 0	138 0	307 0	26 31
	42	16 0	34 0	75 0	170 0	49 27
	50	9 5	20 5	40 5	93 5	88 84
	60	4 5	9 75	19 5	45 5	186 9
40% Glycerol	35	32 0	62 0	120 0	284 0	30 80
	42	17 0	35 0	72 0	178 0	51 13
	50	9 5	20 0	40 5	94 0	90 33
	60	4 5	9 0	19 0	47 0	193 6
60% Glycerol	35	28 5	57 0	124 5	321 0	30 10
	42	15 0	31 5	67 5	195 0	57 06
	50	7 5	15 5	35 0	94 0	110 6
	60	4 5	9 75	19 0	55 5	193 6
80% Glycerol	35	36 0	72 0	147 0		25 09
	42	15 0	33 0	80 0		48 40
	50	10 0	22 0	46 0		83 39
	60	4 0	9 5	21 0		180 7

TABLE III
Hydrolysis of Ethyl Chloracetate

Medium	Temperature in °C	Time for % reaction in minutes				$k_1 \times 10^5$
		5	10	20	40	
20% Glycerol	35	45 0	99 0	201 0	450 0	17 82
	42	27 0	54 0	112 0	249 0	32 65
	50	17 0	32 0	62 0	135 0	58 28
	60	8 0	16 0	30 0	66 0	117 9
40% Glycerol	35	42 0	89 0	177 0	397 0	20 53
	42	25 0	50 0	100 0	226 0	36 13
	50	13 0	26 0	52 0	120 0	71 32
	60	7 0	13 0	26 5	61 0	142 7
60% Glycerol	35	39 0	78 0	157 0	381 0	23 16
	42	21 0	45 0	96 0	225 0	38 72
	50	11 5	23 0	48 0	117 0	77 43
	60	7 0	13 0	25 0	61 0	142 6
80% Glycerol	35	37 0	79 0	156 0	384 0	23 16
	42	21 0	42 0	90 0	240 0	43 01
	50	12 0	25 0	50 0	130 0	73 23
	60	6 0	12 0	24 0	62 0	150 5

TABLE IV
Values of k_1 , E , and Log PZ for Ethyl Acetate in Different Solvents

Solvent	$k_1 \times 10^5$ at 42°	E	Log PZ
20% Glycerol	47 54	16,620	8 2377
40% Glycerol	56 45	15,870	7 7559
60% Glycerol	60 22	14,370	6 7853
80% Glycerol	47 26	17,100	8 5798
60% Dioxane	24 41	16,930	8 1761
60% Alcohol	17 37*	16,200	7 5665

* The value is at 39° 8 and is taken from Hinshelwood and Tamm (?).

TABLE V
Values of k_1 , E and Log PZ for Ethyl Propionate in Different Solvents

Solvent	$k_1 \times 10^5$ at 42°	E	Log PZ
20% Glycerol	49.27	15,880	7.7243
40% Glycerol	51.13	15,250	7.3010
60% Glycerol	57.06	13,900	6.4771
80% Glycerol	48.4	16,130	7.8692
60% Dioxan	19.93	15,960	7.3802

TABLE VI
Values of k_1 , E and Log PZ for Ethyl Monochloracetate in Different Solvents

Solvent	$k_1 \times 10^5$ at 42°	E	Log PZ
20% Glycerol	32.65	15,160	7.0414
40% Glycerol	36.13	15,790	7.5682
60% Glycerol	38.72	14,650	6.8325
80% Glycerol	43.01	15,310	7.2553
60% Dioxan	15.05	16,640	7.7993
60% Alcohol	13.48*	15,300	6.9017

* The value is at 39° 8 and is taken from Hinshelwood and Timm (2)

TABLE VII

Solvent	Viscosity in centipoises at 30° C	Time (mins) taken for 10% reaction at 35° C		
		Ethyl Acetate	Ethyl Propionate	Ethyl Chloracetate
20% Glycerol	1.36	70	72	99
40% Glycerol	2.73	61	62	89
60% Glycerol	7.31	54	57	78
80% Glycerol	34.92	69	72	79
60% Dioxan	1.63	138	162.5	202
60% Alcohol	1.69	406*	.	445*

* The values are at 24° 86 and are taken from Hinshelwood and Timm (2)

An examination of the tables brings out clearly that both the composition of the solvent and the nature of the ester influence the reaction. Some abnormalities are also noticeable, *e g*, an apparently fast reaction in 60% glycerol as compared with other concentrations of glycerol.

The most important influence that must be considered is that of the solvent on the parameters of the reaction velocity equation. It is clear that for the same reaction both *E* and *PZ* vary considerably and are affected to different degrees. The change in value of *E* is of the order of 2.8 kilocalories which is beyond the limits of experimental error while that in *PZ* is even more significant, being several powers of ten.

Following Hinshelwood and Fairclough⁴ $\log PZ$ may be plotted against $\frac{1}{\sqrt{E}}$ (Fig. 1). The curves are not linear and extrapolation to $\frac{1}{\sqrt{E}} = 0$ gives for *PZ* values several powers of ten greater than that corresponding to

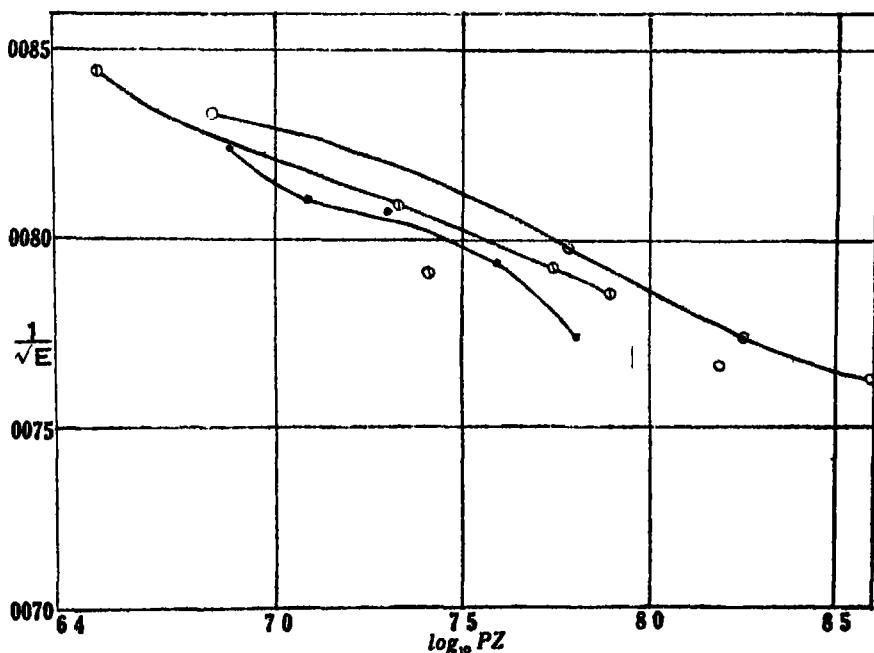


FIG. 1

a gas collision number with $P=1$. At the same time the close correlation between *E* and *PZ* may be seen from the linear character of the *E*— $\log PZ$ curve (Fig. 2).

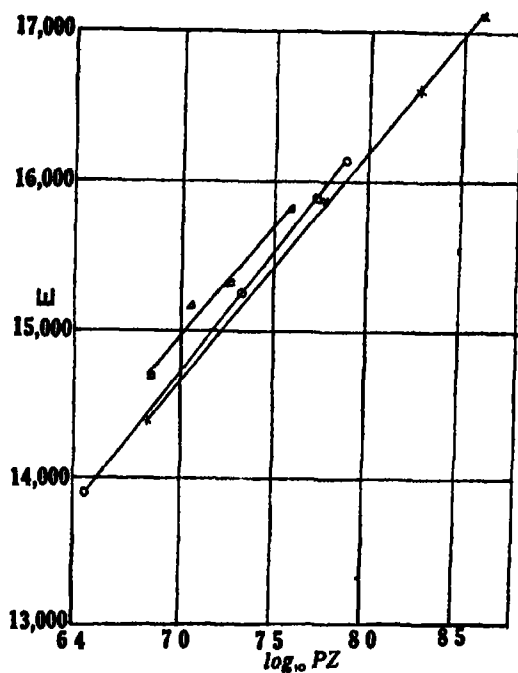


FIG 2

- Ethyl Acetate
 × Ethyl Propionate
 △ Ethyl Chloracetate

Now the whole process can be visualised as involving the principal factors of activation, deactivation and completion of the chemical change Jowett⁵ has shown that the collision frequency in a liquid system exceeds that in a gaseous system and in the derivation of the correction factor the viscosity term appears in the numerator

$${}_1Z_c = \frac{3 \pi \eta \sigma}{2 m_1}$$

when ${}_1Z_c$ is the number of collisions which a solute molecule of mass m_1 and diameter σ makes during one second in a medium of viscosity η .

If every collision were effective and if viscosity were to be the primary factor, one may expect the reaction in 80% glycerol to be the fastest in the present series, whereas the reaction appears fastest in 60% glycerol and the velocity in 80% glycerol is not very different from that in 20% glycerol, though the viscosity is 24 times greater. Considering the ionic nature of the reaction, the dielectric constant of solvent may be expected to greatly

influence the speed of the reaction. With glycerol-water systems, we have consequently to take into account changes in both dielectric constant and viscosity with composition. Data on the dielectric constant of mixtures of glycerol and water are not available but data on variations of viscosity with composition and with temperature are available. The latter alone is inadequate for drawing any quantitative deductions, which must therefore be postponed to a later date. A qualitative comparison is, however, possible. Within the small temperature range investigated, the change in dielectric constant is only about 10% assuming the mixture law to be valid for glycerol-water systems. On the other hand, in the same range, the viscosity changes fourfold, the value at 60° being only a fourth of the value at 35°. The two influences probably work in opposite directions and one may expect a point of maximum velocity in changing from 0% glycerol to 100% glycerol. The position of this maximum will naturally shift with temperature and will vary with the nature of the ester. These changes can be observed in two ways—(1) plotting the time taken for a definite percentage of the reaction (say 20%) against the composition of the medium (Fig 3), and (2) plotting change of E with composition of the medium (Fig 4).

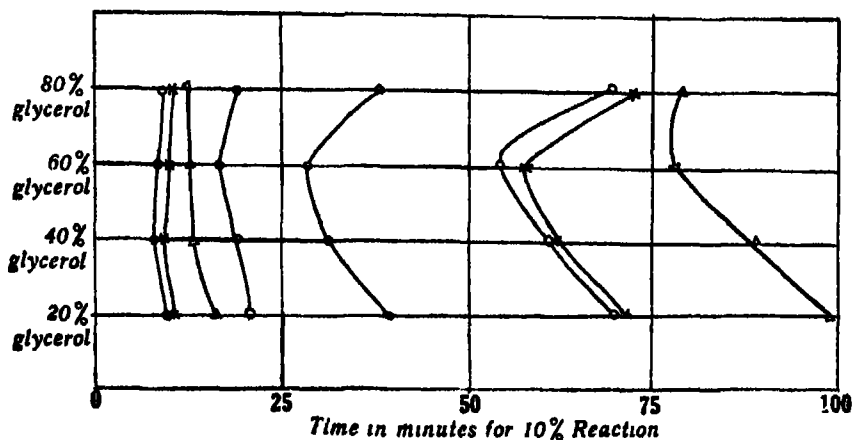


FIG 3

- Ethyl Acetate
- × Ethyl Propionate
- △ Ethyl Chloracetate

It will be noticed from Fig 3 that a parabolic curve is obtained which flattens out with increase of temperature, the position of maximum velocity shifting from about 60% glycerol at 35° C to 40% glycerol at 60° C. A more complete picture is possible only with larger temperature ranges and intermediate compositions for the medium.

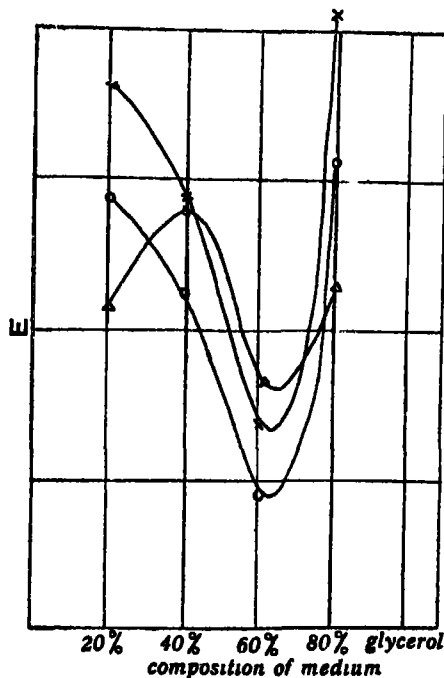


FIG 4

Fig. 4 brings out another aspect. Ethyl acetate and ethyl propionate are affected in the same way by change of solvent. Except for a slight displacement, the shape of the curve is the same, the reaction showing a minimum value of E in the 60% glycerol region. Chloroacetic ester on the other hand appears to behave differently, the curve showing a maximum and a minimum. This difference is probably only one of degree and an explanation is possible only after a more complete investigation of the change with intermediate glycerol concentrations in the solvent. These will form the subject of a later communication. The solvent influences the reaction both by increasing Z and by providing a polar environment that facilitates the breaking up of the transition-complex.

It is interesting to compare also, the velocity of the reaction in glycerol-water with that in dioxan-water and alcohol-water systems. The reaction is slowest in alcohol though the dielectric constant of alcohol is much greater than that of dioxan and the viscosity is slightly greater (Table VII). This must be attributed to the fact that ethyl alcohol is also a product of reaction and the presence of an environment of alcohol molecules stabilizes the transition complex. Since the rate-determining step involves the

breaking up of this complex, an apparently slow reaction is the result. In dioxan, this complication is absent and the reaction is much faster. Both these solvents have a lower dielectric constant and a much lower viscosity than glycerol-water systems and the comparatively faster reaction is easily understandable. Noteworthy also is the fact that though 20% glycerol is less viscous than either 60% dioxan or 60% alcohol, the reaction in that solvent is faster. The difference must be traced to the higher dielectric constant. Mention may be made here of the peculiar solvent influence in the pyridine methylodide reaction in mixed solvents³

One of the authors (S K) thanks the authorities of the Annamalai University for a studentship which enabled him to undertake the experimental work

Experimental

The experimental procedure was similar to that described in Part I. Glycerol (bidistilled, s g 1 23 for analysis, Kahlbaum) was used without further purification)

Summary

The kinetics of acid hydrolysis of ethyl acetate, ethyl propionate and ethyl chloracetate in glycerol-water system has been studied. Both viscosity and dielectric constant influence the reaction and a close correlation of the parameters of the reaction velocity equation is noticed

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ISOLATION AND CONSTITUTION OF QUERCETAGITRIN, A GLUCOSIDE OF QUERCETAGETIN

BY P SURYAPRAKASA RAO AND T R SESHADRI
(From the Department of Chemistry, Andhra University, Waltair)

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THERE has been some confusion in the past regarding the use of the common and the botanical names of the flowers of the Tagetes. The correct designation should be *T. erecta* for the African Marigold and *T. patula* for the French Marigold¹

The flowers of the African Marigold (wrongly named as *T. patula*) were first examined by Latour and Magnier De La Source². They were extracted with boiling 85% alcohol, and the flavonol, quercetagetin was isolated in an impure state by concentrating the extract. Later Perkin³ carried out a more detailed investigation. The alcoholic extract of the flowers was concentrated, diluted with water and extracted with ether which dissolved the free quercetagetin. Though Perkin realised that the aqueous solution contained a glucoside of the flavonol, he did not attempt to isolate it but directly hydrolysed it for reasons of economy to produce more quercetagetin. Thinking that Perkin and others examined the flowers of *T. patula*, Mahal⁴ recently studied the flowers of *T. erecta* (wrongly designated as French Marigold) and showed that they contained the same pigment. He too did not attempt to isolate the glucoside. It is obvious that both Perkin and Mahal investigated the same species, *T. erecta*, Perkin having given the wrong botanical name and Mahal the wrong common name. This presumption of ours has been confirmed by the examination of the flowers of *T. patula* also, whose chemical composition is very different. The present investigation has been undertaken with a view to isolate the glucoside and establish its constitution, and these objects have been achieved.

The chemical examination of the petals of *T. erecta* was carried out on the same general lines as had been adopted in the case of the cotton flowers⁵. When the alcoholic extract was concentrated and allowed to stand, a yellow crystalline solid was obtained, and this was found to consist of the glucoside of quercetagetin, now called quercetagitrin. The mother-liquor was diluted with water and ether extracted, whereby quercetagetin was isolated. The

neutral and the basic lead acetate fractions were insignificant, and hence they were not worked up

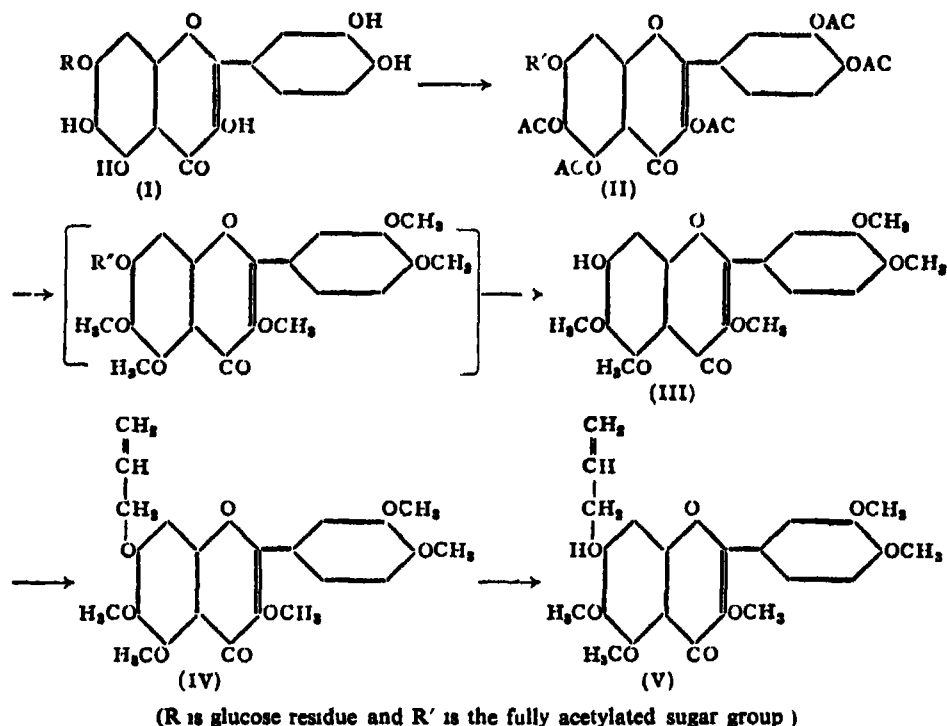
Quercetagitrin is a monoglucoside ($C_{31}H_{30}O_{13}$) yielding on hydrolysis one molecule of glucose and one of quercetagetin. It crystallises in the form of yellow needles and melts with decomposition at $236-38^\circ$. Its non-acetyl derivative melts at $225-27^\circ$. Sodium hydroxide readily dissolves the substance to yield a yellow solution, and ferric chloride imparts a brownish-green colour to an alcoholic solution. With alkaline buffer solutions, the most prominent colour of the glucoside is pink, and this test enables the substance to be easily distinguished from its aglucone, quercetagetin which gives a transient green and a final brown or brown-red as the characteristic colours.

The new glucoside is isomeric with gossypitrin and cannabiscitrin⁶. It gives a brick-red precipitate with lead acetate and is hydrolysed with difficulty by acids, showing thereby that it is not a 3-glucoside. It undergoes ready oxidation in cold alkali to produce protocatechuic acid, and hence the sugar group should be present in the benzopyrone ring. To definitely establish its position the glucoside is completely methylated through its acetyl derivative⁷ (II) and the product hydrolysed with a view to identify the resulting pentamethyl quercetagetin (III). This pentamethyl ether cannot have the free hydroxyl group in either 3- or 3'- or 4'-position since the glucoside does not have the sugar unit in those positions. Further the compound gives rise to veratric acid on oxidation in boiling 50% potash. As shown in the following table it is entirely different from 3, 6, 7, 3', 4'-pentamethyl quercetagetin originally prepared by Perkin³ by the methylation of the flavonol and later synthesised by Baker, Nodzu and Robinson⁸ during the course of the synthesis of quercetagetin.

	Solubility in cold sodium hydroxide	Colour with ferric chloride	Melting point
3, 6, 7, 3', 4'-pentamethyl quercetagetin	Almost insoluble	Intense olive green colour	$159-60^\circ$
The new pentamethyl quercetagetin	Easily soluble	No prominent colour	$234-35^\circ$

Hence the free hydroxyl group is not in position 5; it should be in either 6 or 7 position. To settle this point, the pentamethyl ether is allylated and the allyl ether (IV) subjected to Claisen Rearrangement, when the allyl group undergoes smooth migration (V). This is possible only if the allyl group were originally present in the 7th and not the 6th position as otherwise the

migration cannot occur for want of a free ortho- or para-position. Hence the free hydroxyl group should have been in position 7 in the pentamethyl ether and so the glucoside should be a 7-glucoside (I). The changes involved are diagrammatically represented below.



Experimental

Isolation of Quercetagitrin—6 Kg. of the dry petals of the African Marigold flowers were extracted with methylated spirit in batches of 500 g. Each batch was refluxed with alcohol two times, each treatment lasting for about 12 hours. The combined alcoholic extract was concentrated by distillation to about 1000 c.c. The waxes and the resins that separated out were carefully filtered off through fluted filters, and after the addition of a few drops of toluene, the concentrate was allowed to stand for a long time. After four months some yellow crystalline solid began to appear. The supernatant liquid too became a thick syrup by the separation of further quantities of wax and resin, and consequently the filtration of the pigment became extremely slow and difficult. The residue which was brown in colour and sticky to the touch was thoroughly washed with alcohol, when all the impurities were removed and the solid assumed a golden yellow colour.

The mother-liquor continued to deposit more and more of the yellow substance, which was filtered at intervals, and the deposition was complete towards the end of six months. After the preliminary purification with alcohol as stated above, the compound was boiled with chloroform in order to remove carotinoid material. Now it became almost pure, and was found to be practically insoluble in boiling water, alcohol or even acetic acid, though the impure stuff readily went into solution in hot water. It was finally crystallised from aqueous pyridine, when it came out as golden yellow glistening needles and rectangular plates melting at $236-38^{\circ}$ (decomp). The yield was 8 g. [Found in the air-dried sample C, 48.5, H, 4.8, $C_{21}H_{20}O_{13}$, $2H_2O$ requires C, 48.8, H, 4.6%. Found in the sample dried at 120° *in vacuo*: C, 52.3; H, 4.6, $C_{21}H_{20}O_{13}$ requires C, 52.5, H, 4.2%]

Isolation of Quercetagenin—The alcoholic mother-liquor remaining after the separation of the glucoside was diluted with a large volume of water and then extracted with ether. On distilling off the solvent, the extract yielded a good amount of a dark brown viscous liquid. When a small quantity of water was added, the liquid changed into a yellow crystalline solid mixed with some resin. The mixture was extracted with cold alcohol which dissolved preferentially the pigment and not the resin. On concentration the alcoholic extract deposited a yellow solid. Further purification was effected by crystallisation from acetic acid, when the substance was obtained as clusters of short needles and plates melting at $314-16^{\circ}$. The yield was 10 g. [Found in the air-dried sample C, 50.5, H, 4.2; $C_{18}H_{10}O_8$, $2H_2O$ requires C, 50.9, H, 4.0%. Found in the specimen dried at 120° *in vacuo*: C, 56.3, H, 3.5, $C_{18}H_{10}O_8$ requires C, 56.6, H, 3.1%]. On acetylation with acetic anhydride and anhydrous sodium acetate the substance yielded an acetyl derivative which was found to melt at $209-10^{\circ}$ and agree with acetyl quercetagenin in all its properties.

Properties of the Glucoside—Quercetagenin was obtained as fine short needles when rapidly crystallised, but on slow crystallisation, it came out as needles and narrow rectangular plates. It produced a brick-red precipitate with lead acetate, and with ferric chloride a brownish green colour. When a small quantity of sodium hydroxide solution was added, the substance immediately dissolved forming a yellow solution. On shaking with air, the yellow colour rapidly changed to brown, and a dark brown precipitate separated out. With alkaline buffer solutions of pH value below 10, the colour changes were slow and not very prominent; but with solutions of higher pH value, the characteristic colour was pink. The formation of this pink colour enables the substance to be distinguished from its aglucone

which gives on the other hand a transient green and a more stable brown or brown-red

pH	Quercetagetin	Quercetagitritin
9.2	Dissolved to produce a lemon-yellow solution. The colour changed to greenish-yellow within 2 minutes and greenish-brown after 10 minutes. The brown colour slowly intensified and became very prominent the next day.	Immediately dissolved forming a yellow solution. The yellow colour changed slowly to brownish-yellow and the solution assumed a brownish-pink colour after half an hour. After two hours, it was light pink which gradually intensified. After 6 hours the pink colour began to disappear slowly. Even the next day, this tinge was still noticeable.
10.4	Same changes as above but very rapid.	The same changes as above but more rapid. The brownish-yellow colour appeared after 5 minutes and changed to brownish-pink within another minute. The pink colour became prominent after 10 minutes.
11.0	An immediate lemon-yellow solution which became greenish-yellow within half a minute, greenish-brown within a minute and pure brown within 5 minutes. The transition colour between greenish-yellow and greenish-brown was pure green itself. The solution became brownish-red after half an hour and reddish-brown the next day.	The same changes as above but more quickly. The pink was very prominent even after 5 minutes.
12.2	Same changes as in the previous case but very quick. The reddish-brown appeared even within 5 minutes and changed to brownish-red after 10 minutes.	In this case the colour changes were very quick, yellow—brownish-yellow—brownish-pink—pink. The final shade was noticeable even within 3 minutes and was very prominent after 5 minutes. The next day, the solution was still pink.

Hydrolysis of the Glucoside—The substance (2 g) was hydrolysed by boiling with 7% sulphuric acid (100 c.c.) After heating for a few minutes, the solid went into solution, and within half-an-hour another yellow solid separated out, giving rise to bumping. The contents were, therefore, heated for an hour and a half more on a boiling water-bath. After cooling, the precipitate was filtered and the filtrate extracted with ether to completely recover the aglucone. The ether-extract, after the distillation of the solvent, yielded a small amount of the substance. The two samples of the aglucone were mixed together, dried in air and weighed accurately. After recording the yield, the solid was crystallised from dilute alcohol, when it came out as short needles and plates melting at 315–16°. [Found in the air-dried sample. C, 50.5, H, 4.0; $C_{18}H_{16}O_8$, 2 H_2O requires C, 50.9; H, 4.0%.]

The substance was identified as quercetagetin and this was confirmed by preparing its acetyl derivative and comparing it with an authentic sample of acetyl quercetagetin

The acid solution left after the removal of the aglucone was made up to 120 c c and divided into two equal portions. One part was further diluted, neutralised with barium carbonate, and treated after concentration to a small bulk with phenyl hydrazine in dilute acetic acid. When the mixture was heated on a water-bath, the osazone separated out. After crystallisation from alcohol, it was identified as glucosazone from a study of its crystalline structure and the melting point ($204-06^{\circ}$). The other part of the sugar solution was made alkaline by the addition of sodium carbonate and the glucose estimated by titration against standard Fehling solution

The amounts of the aglucone and the glucose produced as a result of the hydrolysis of the glucoside were calculated [Found Aglucone, 68.0; Glucose, 34.3%, $C_{21}H_{20}O_{13}$, $2 H_2O$ requires Aglucone ($C_{15}H_{10}O_8$, $2 H_2O$) 68.6, Glucose, 34.9%]

Alkaline Oxidation of the Glucoside Isolation of Veratric Acid—Quercetagitritin (0.5 g) was treated with 50% aqueous potash (15 c c), when it dissolved immediately to form a blood-red solution. On leaving exposed to air with occasional shaking for 24 hours, the solution became opaque and brown. It was then directly treated, after dilution, with excess of dimethyl sulphate (20 c c) in small quantities. After shaking for an hour, the contents were heated on a water-bath for about 30 minutes to complete the methylation and decompose the excess of the methylating agent. The solution was then acidified and ether extracted. A crystalline solid was obtained on evaporating the solvent from the ether extract. It was purified by dissolving in sodium bicarbonate solution and precipitating with hydrochloric acid. When crystallised from aqueous alcohol, it was obtained as colourless needles melting at $183-84^{\circ}$, and was found to be identical with veratric acid.

Acetylation of the Glucoside: Nonaacetyl Quercetagitritin—A small quantity of the glucoside was acetylated by boiling with acetic anhydride and anhydrous sodium acetate. The acetyl derivative was crystallised from glacial acetic acid, when it was obtained as colourless needles melting at $225-27^{\circ}$ [Found C, 54.8, H, 4.8, $C_{21}H_{11}O_4$ ($OCO CH_3$)₉ requires C, 54.5, H, 4.4%]

3, 5, 6, 3', 4'-Pentamethyl Quercetagetin—The acetyl quercetagitritin (0.5 g) was dissolved in acetone (25 c c) and treated alternately with dimethyl sulphate (10 c c) and 20% sodium hydroxide (10 c c) in small quantities,

The mixture was shaken vigorously after each addition, considerable amount of heat developed during the course of the reaction. Further quantities of the methylating agent (5 c c) and the alkali (5 c c) were then added, and finally the medium was made definitely alkaline by the gradual addition of more alkali (15 c c). The next day the mixture was refluxed for an hour on the water-bath, and the acetone present was then distilled off. Subsequently the clear alkaline solution was just neutralised and then the required amount of concentrated sulphuric acid was added to it so as to make it 7% in the acid content. After boiling under reflux for 2 hours, the clear solution was cooled in the refrigerator, when a colourless crystalline solid was deposited. It was filtered and the filtrate on ether-extraction yielded a little more. On crystallisation from dilute alcohol, it was obtained as long plates and needles melting at 234–35°. It was easily soluble in sodium hydroxide and it gave no colour with ferric chloride. The yield was 0.3 g. [Found C, 61.8, H, 5.3, OCH_3 , 39.4, $\text{C}_{18}\text{H}_{14}\text{O}_2$ (OH) (OCH_3)₅ requires C, 61.9, H, 5.2, OCH_3 , 40.0%]. By subjecting it to alkaline oxidation using boiling 50% aqueous potash in a silver flask, the pentamethyl ether gave rise to veratric acid.

3':4'.3.5.6-Pentamethyl-7-allyl Quercetagetin—The pentamethyl quercetagetin (0.5 g) was dissolved in dry acetone (50 c c), anhydrous potassium carbonate (2 g) and excess of allyl bromide (2 c c) were added to the solution and the mixture boiled under reflux on a water-bath for about 6 hours. The potassium salts were then filtered off and all the solvent was completely removed by distilling the clear solution, when a brown-coloured oil was left behind. It was dissolved in ether, and the solution extracted with 5% sodium hydroxide to remove any unattacked pentamethyl quercetagetin. On the removal of the solvent, the ethereal solution yielded again only an oil, which, however, was much less coloured and turned solid after the addition of a little water and leaving overnight in the ice-chest. It was finally purified by crystallisation from dilute alcohol using a little animal charcoal, and was obtained as almost colourless needles. It sintered at about 118° and melted at 122–24°. [Found in the sample dried at 120° *in vacuo*: C, 64.2, H, 5.7, $\text{C}_{23}\text{H}_{24}\text{O}_8$ requires C, 64.5, H, 5.5%]. The compound did not dissolve in dilute sodium hydroxide and gave no colour with ferric chloride. The yield of the pure product was 0.3 g.

3':4'.3.5.6-Pentamethyl-8-allyl Quercetagetin—The above pentamethyl-7-allyl quercetagetin (0.3 g) was taken into a pyrex filter-tube provided with a tight-fitting rubber stopper. The tube was then exhausted as much as possible using a "Cenco" pump for 15 minutes and then heated on

an oil-bath at 195–200° for 1½ hours. By this treatment a brown semi-solid was obtained, which completely solidified on the addition of a small quantity of water. It crystallised from dilute alcohol (animal charcoal) as colourless narrow rectangular plates melting at 188–90° [Found C, 64.2, H, 5.8, $C_{28}H_{24}O_8$ requires C, 64.5; H, 5.5%]. It was freely soluble in dilute sodium hydroxide. The yield of the pure substance was 0.2 g.

Summary

Quercetagitrin, a monoglucoside of quercetagetin, has for the first time been isolated from the flowers of the African Marigold (*Tagetes erecta*). It is not a 3-glucoside since it gives a red precipitate with lead acetate and does not undergo easy hydrolysis with acids. Further it is easily oxidised in cold alkali, and after methylation the products of decomposition yield veratric acid. The glucose group, therefore, is not present in the side phenyl nucleus. By complete methylation and subsequent hydrolysis of the glucoside, a pentamethyl quercetagetin is obtained. This ether is a new compound, and differs from 3, 6, 7, 3', 4'-pentamethyl quercetagetin in all its properties, and hence the free hydroxyl group in it is in either the 6th or the 7th position. The allyl ether of this new pentamethyl quercetagetin smoothly undergoes the Claisen Rearrangement, indicating thereby that the ortho-position with respect to the allyloxy group is unsubstituted. Hence the allyl ether should be 3, 5, 6, 3', 4'-pentamethyl-7-allyl quercetagetin, and the new pentamethyl ether should have the constitution of 3, 5, 6, 3', 4'-pentamethyl quercetagetin. Consequently quercetagitrin is the 7-glucoside of quercetagetin.

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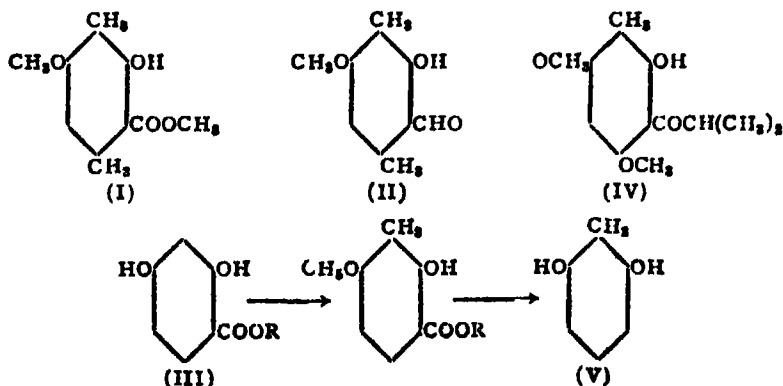
NUCLEAR METHYLATION OF β -RESORCYLIC ALDEHYDE

BY T R SESHADRI AND V VENKATESWARLU

(From the Department of Chemistry, Andhra University, Waltair)

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UNDER conditions of methylation, certain poly-hydroxy phenyl derivatives exhibit a tendency to undergo substitution in the benzene nucleus. This phenomenon is known as nuclear methylation. Not only is the chemistry of this reaction interesting, but it has also useful applications in synthetic work. For instance, methyl orsellinate was found to be directly and conveniently methylated with the formation of methyl rhizonate¹ (I). In a similar manner rhizonic aldehyde (II) has been prepared readily by the methylation of orcylic aldehyde. Early work of Perkin³ and of Herzog *et al*⁴ on the methylation of β -resorcylic acid and ester (III) has been reviewed in the above-mentioned paper by Robinson and Shah.¹ Their ideas have been confirmed by Jones and Robertson⁵ by careful comparison of some of the important products of methylation with substances obtained by definite methods of synthesis.

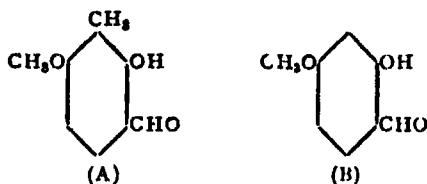


Kauffler⁶ and Perkin³ found that nuclear ethylation is a much less facile process. Robinson and Shah,¹ however, were able to effect nuclear ethylation of the methyl ester of resorcylic acid using large excess of the reagents. Nuclear methylation of resocetophenone was effected by Greger,⁷ Wechler⁸ and Crabtree and Robinson⁹ and nuclear ethylation was carried out by Robinson and Shah.¹ The constitution of the products was drawn only

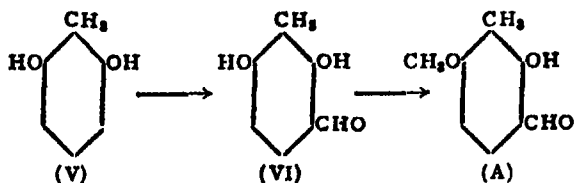
from analogy with the similar reaction with resorcylic acid and ester. The subject was subsequently reinvestigated by Rangaswami and Seshadri,¹⁰ who confirmed the structures by unequivocal synthesis and by preparation of derivatives. They employed for this purpose resacetophenone and ω -methoxy-resacetophenone. An observation regarding nuclear methylation of a phloroglucinol derivative has been recently made by Hems and Todd.¹¹ Using phloroisobutyrophenone, they found that the reaction took place even under very mild conditions by boiling the substance in acetone solution with methyl iodide and potassium carbonate, bæckeol (IV) was thus obtained. This may be taken as an instance of very facile nuclear methylation.

The following is an account of past work relating to the nuclear methylation of β -resorcylic aldehyde. Tiemann and Parrisius¹² obtained a compound (A) melting at 62–63° by two methods: (i) by the action of chloroform and alkali on mono-methyl resorcinol, and (ii) by the methylation of β -resorcylic aldehyde with methyl iodide and alcoholic potash. They assigned to it the structure of 2-hydroxy-4-methoxy-benzaldehyde and this has been shown to be wrong by subsequent work. Claisen and Eisleb¹³ showed that by employing methyl iodide and potassium carbonate for the methylation of β -resorcylic aldehyde, two compounds could be isolated: (i) melting at 62–63° and identical with (A) and (ii) melting at 41–42° (B). The mixture of these two products could be separated by taking advantage of their difference in volatility with steam under different conditions; compound (A) distilled over from a faintly alkaline solution and subsequently after rendering the solution acid, compound (B) could be distilled. The above work was confirmed by OTT and Nauen¹⁴ who further showed that methylation of β -resorcylic aldehyde with methyl iodide and alcoholic potash gave compound (A) along with a small quantity of (B), whereas when dimethyl sulphate or methyl bromide and aqueous potash were employed, compound (B) was exclusively formed. The constitution of compound (B) was established by them as 4-O-methyl-resorcylic aldehyde from careful elementary analysis and comparison with a sample obtained from natural products (e.g., from the root of chlorocodon from Natal isolated by Goulding and Pelly).¹⁵ It is now known to occur widely in the following plants: (i) *Decalepis Hamiltonii* (Srinivasa Rao and Sesha Iyengar¹⁶), (ii) *Periploca Gracea* (Solacoin, Mavrodin and Hermann¹⁷), (iii) *Hemidesmus indicus* (Dutta, Ghosh and Chopra¹⁸). Compound (A) was subsequently taken to be nuclear methylated homologue of (B) and it was assumed to have the structure of 2-hydroxy-3-methyl-4-methoxy-benzaldehyde; this assumption was based on analogy with similar resorcinol derivatives. Its formation in small amounts in the experiments of Tiemann and Parrisius¹² using chloroform, alkali and mono-methyl resorcinol was

difficult to explain OTT and Nauen¹⁴ were of the opinion that the mono-methyl resorcinol employed by these authors probably contained 2-methyl-resorcinol. But the explanation does not seem to be satisfactory and the original observations may require revision

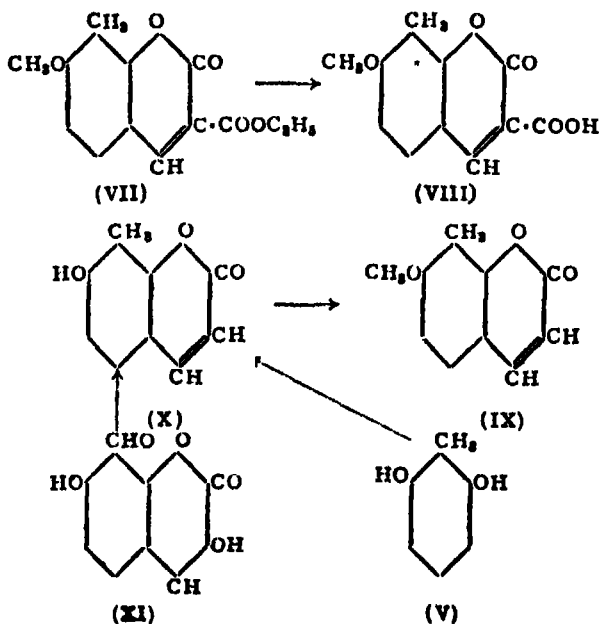


The methods employed by previous workers for effecting nuclear methylation of β -resorcylic aldehyde have not yielded satisfactory results and the constitution of the product has not been established by independent synthesis. OTT and Nauen¹⁴ treated a solution of β -resorcylic aldehyde and methyl iodide in methyl alcohol with finely powdered potassium hydroxide during the course of 12 days. They obtained compound (A) in low yields and it had to be separated from a small quantity of 4-O-methyl-resorcylic-aldehyde. A rapid and convenient procedure has now been worked out and under these conditions (see experimental part) only one product, compound (A) melting at 64–65°, is obtained. The constitution of this compound, as 2-hydroxy-3-methyl-4-methoxy-benzaldehyde has been established by two independent methods. (i) it has been synthesised, starting from 2-methyl-resorcinol (V) according to the method of Jones and Robertson⁵ and the synthetic product compared with the sample obtained by methylation of β -resorcylic aldehyde. The two are identical.

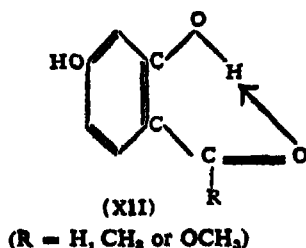


(ii) Compound (A) was condensed with diethyl malonate using piperidine as the condensing agent. The coumarin-3-carboxylic ester (VII) thereby obtained was hydrolysed and the product (VIII) decarboxylated. The final coumarin (IX) thus obtained was found to be 8-methyl-7-methoxy-coumarin, by comparison with a sample obtained independently by synthesis as given below. 2-Methyl-resorcinol (V) was condensed with malic acid to form 8-methyl-7-hydroxy-coumarin (X). The same compound was also obtained by the reduction of 8-aldehydo-7-hydroxy-coumarin (XI) (Spaeth¹⁸) with hydrogen using palladium charcoal as catalyst. It readily underwent

methylation with methyl iodide and potassium carbonate to yield 8-methyl-7-methoxy-coumarin (IX). Thus it is clear that the nuclear position involved in the methylation of β -resorcylic aldehyde is position 3, and that of the two hydroxyl groups, only that present at 4 undergoes ether formation.



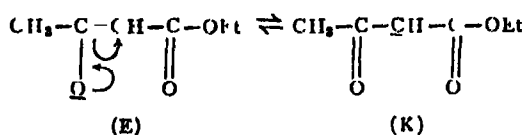
In the examples of nuclear methylation discussed in the previous pages, it should be noted that they come under the category of polyhydroxy carbonyl compounds. The same characteristics of the reactions are observed throughout. Nuclear position 3 with respect to the carbonyl group is the reactive one. Regarding the hydroxyl groups, one of these ortho to the carbonyl group is left unmethylated. It is well known that all these hydroxy-carbonyl compounds are chelated and this chelation has a tendency to cause fixation of the benzene double bonds as shown in (XII).



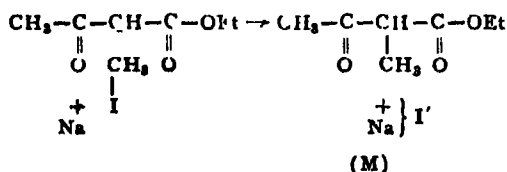
The existence of chelation may account for the non-methylation of the ortho-hydroxyl group and it may also explain the high reactivity of position 3.

From a study of the nuclear methylation of resacetophenone, Crabtree and Robinson⁹ have advanced the following regarding the mechanism of the reaction. These authors indicated that the nuclear methylation of resacetophenone is a reaction of the alkali metal derivatives of the original ketone itself (not of paeanol, the mono-methyl ether) and that it is favoured by an excess of alkali. They found that 4-O-methyl-resacetophenone does not undergo nuclear methylation under the above conditions.

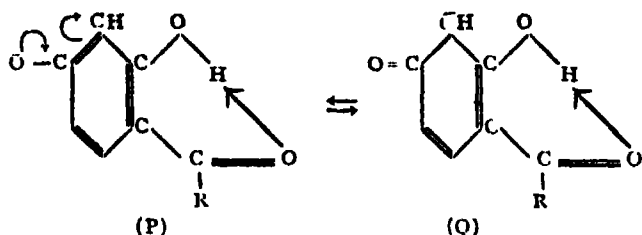
The analogy between the above nuclear methylation and the C-alkylation of ethyl-aceto-acetate seems to be obvious. In both cases the primary cause of the reaction is the existence of an anionoid carbon atom. In the presence of sodium (or potassium) alkoxide the following (E) and (K) may be said to be in equilibrium when ethyl-aceto-acetate is involved



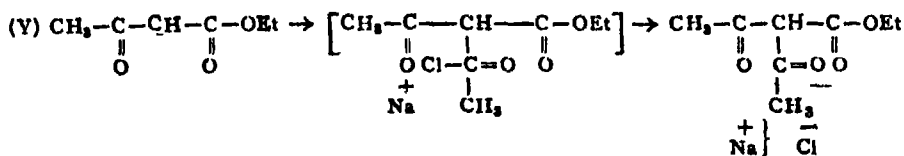
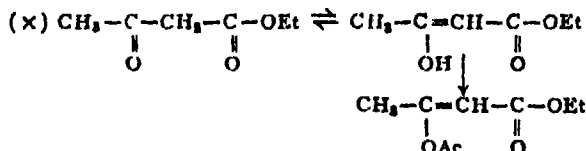
Though (K) may be the lesser component owing to the higher reactivity of the anionoid carbon as compared with the more stable anionoid oxygen, reaction with methyl iodide takes place predominantly with (K) leading to C-methylation (M)



In the case of carbonyl derivatives of resorcinol as shown in (XII), the existence of an extra double bond between the C=O and the carbon atom concerned in no way alters the situation. Under the conditions of methylation adopted (P) and (Q) are obviously in equilibrium and nuclear methylation takes place quite analogous in mechanism to that just outlined, with the only difference that the hydrogen attached to the 3 carbon finally migrates to the oxygen to give a phenol. This explains why preliminary methylation of the para-hydroxyl group is injurious to nuclear methylation (Crabtree and Robinson⁹). Further it may be remarked that existence of chelation may be expected to increase the electron pull towards the carbonyl, thus facilitating the polarisation as indicated in (P) and eventually nuclear methylation. The conditions employed seem to be very conducive for the existence of chelate structure, thus preventing the methylation of the ortho-hydroxyl group.



It has been the practice to view C-alkylation of ethyl-aceto-acetate as involving addition of methyl iodide at the double bond of the enol ²⁰ This does not seem to be tenable since there is no positive proof of such addition and since there is no other example where methyl iodide has been proved to add on to the double bonds. On the other hand, all its reactions seem to be characterised by the ready elimination of iodide ions after attack at the unstable anionoid carbon. In this connection it may be mentioned that acid chlorides react with the sodium derivative of ethyl-aceto-acetate similarly to form C-acyl derivatives whereas when the free compound itself is employed in the presence of pyridine O-acyl derivatives are formed ²¹ The latter is obviously simple ester formation in which the enol takes part and the keto-isomer is unreactive (X). The reaction with the metal derivative is again due to attack on the anionoid carbon (Y). Definite cases of addition of acyl chlorides to double bonds are not known.



Experimental

Nuclear methylation of β -resorcylic aldehyde. 2-hydroxy-3-methyl-4-methoxy-benzaldehyde (A)—To a solution of caustic potash (7.5 g, 4.5 mols) in anhydrous methyl alcohol (40 c.c.) β -resorcylic aldehyde (5 g) was added. The solid dissolved slowly to form a clear solution which was deep brown in colour. On cooling it in a freezing mixture, it set into a solid mass. Enough methyl alcohol was therefore added to obtain a clear solution again at this low temperature and then the mixture was treated with excess of ice-cold methyl iodide (30 c.c., 7 mols.) in one lot.

The contents were then well shaken for about half an hour, the flask being immersed in freezing mixture and kept well-stoppered. Subsequently it was allowed to assume laboratory temperature slowly and to stand overnight. Next morning, crystals of potassium iodide had separated at the bottom and a clear solution was found above. The mixture was gently boiled under reflux for 8 hours, cooled and poured into ice-water and left overnight. As much of the alcohol as possible was then removed by distillation under reduced pressure and the highly coloured residue was subjected to steam-distillation. A colourless oil came over and soon solidified. When recrystallised from methyl alcohol it was obtained as colourless elongated rectangular plates melting at $64-65^{\circ}$ [Found C, 64.9; H, 6.2, $C_9H_{10}O_3$ requires C, 65.1; H, 6.0]. The yield of the pure product was 1.5 g. It does not undergo condensation with acetic anhydride and sodium acetate under the conditions of Perkin's reaction.

2,4-Dihydroxy-3-methyl-benzaldehyde (VI) was made according to the method of Jones and Robertson with the modification that zinc cyanide was used in the place of hydrogen cyanide.

A solution of 2-methyl resorcinol (2 g) and zinc cyanide (5 g) in anhydrous ether (40 c.c.) was cooled in ice and saturated with hydrogen chloride. The aldimine hydrochloride began to separate after thirty minutes. The current of the gas was, however, continued for 4 hours, at the end of which the solid was separated, washed with more ether and decomposed with water (35 c.c.) by heating on a boiling water-bath. The aldehyde separated out from water in colourless rhombic prisms melting at 150° with slight sintering at 137° . The yield of the product was 1.6 g.

The above dihydroxy-aldehyde (VI) was methylated using excess of methyl iodide and potassium carbonate in boiling acetone solution. Almost quantitative yield of the 4-methyl ether was obtained and it crystallised from dilute alcohol in plates melting at $64-65^{\circ}$. It was found to be identical with the sample obtained from the nuclear methylation of β -resorcylic aldehyde.

Ethyl-7-methoxy-8-methyl-coumarin-3-carboxylate (VII)—The nuclear methylation product (A) (1 g, 1 mol) was mixed with diethyl malonate (1.4 g, 1.4 mol) and cooled in ice. Piperidine (10-15 drops) was then added. (Cooling was found necessary as otherwise heat was developed causing considerable resinification.) The mixture was allowed to stand overnight and to attain room temperature slowly. The resulting solid was treated with dilute hydrochloric acid, filtered and recrystallised from alcohol. It came out as colourless thin rectangular plates melting at $159-60^{\circ}$. In neutral alcoholic solution it emitted a violet fluorescence and in concentrated

sulphuric acid the fluorescence was green [Found C, 64.3, H, 5.5, $C_{14}H_{14}O_6$ requires C, 64.1, H, 5.3%] Yield 1.5 g

7-Methoxy-8-methyl-coumarin-3-carboxylic acid (VIII)—The above ester (1 g) was treated with excess of alcoholic potash (20 c.c. of alcohol containing 3 g of potassium hydroxide) and allowed to stand for 3 days. The clear solution was then diluted with water and acidified with dilute hydrochloric acid. The precipitated solid was filtered and purified by dissolution in aqueous sodium carbonate and reprecipitation. When finally crystallised from alcohol it came out as light yellow needles and rectangular plates melting at 211–212°. It resembled the ester very closely in the nature of its fluorescence [Found C, 61.4, H, 4.6; $C_{13}H_{10}O_5$ requires C, 61.6, H, 4.3%]

7-Methoxy-8-methyl-coumarin (IX)—The above carboxylic acid (0.5 g.) was heated with quinoline (20 c.c.) and copper bronze (1 g.) for $\frac{3}{4}$ hour at 150–60° in an oil-bath. After cooling, the mixture was treated with excess of ether and the solution quickly filtered. Ether was then distilled off, the residue was treated with excess of dilute hydrochloric acid and the mixture was repeatedly shaken with ether. The ether extract was washed free from acid with aqueous sodium bicarbonate and then water and finally evaporated. The resulting solid was extracted with petroleum ether, whereby some resin was left behind. The petroleum extract was evaporated and the solid residue crystallised from alcohol. Colourless rectangular prisms and plates were thus obtained melting at 122–23°. The substance gave a weak violet fluorescence in alcohol and a bluish green fluorescence in concentrated sulphuric acid. It was found to be identical with the sample of 7-methoxy-8-methyl-coumarin prepared from 2-methyl-resorcinol as given below [Found C, 69.7, H, 5.5; $C_{11}H_{10}O_3$ requires C, 69.5, H, 5.3%]

7-Hydroxy-8-methyl-coumarin (X). Method I—An intimate mixture of 2-methyl-resorcinol (1 g, 1 mol), malic acid (1.2 g, 1 mol), and concentrated sulphuric acid (2.5 c.c.) was heated in an oil-bath maintained at 120° until effervescence ceased (1½ hours). After cooling, the product was poured with stirring into excess of crushed ice and left overnight. The solid was then filtered and extracted with ether. By this treatment, a small quantity of insoluble resin was removed. After distilling off the solvent the residue was recrystallised from alcohol, when colourless triangular prisms melting at 231–232° were obtained. The substance gave a pale blue fluorescence in neutral alcoholic solution and it was bright bluish in alkaline solution. In concentrated sulphuric acid the colour of the fluorescence was bluish green [Found: C, 72.6, H, 4.4; $C_{10}H_8O_3$ requires C, 72.7; H, 4.6%.]

Method II : Reduction of 7-hydroxy-coumarin-8-aldehyde (XI)—A solution of the aldehyde in glacial acetic acid was treated with palladium charcoal and shaken in an atmosphere of hydrogen till two molecular proportions of the gas were absorbed. The solution was then filtered and the solvent removed as far as possible by distillation under reduced pressure. The residue was then treated with water, the acetic acid remaining behind was neutralised with sodium carbonate and the mixture repeatedly extracted with ether. The ether solution was then shaken with saturated sodium bisulphite to remove any unreduced aldehyde and subsequently washed with water. After distilling off the solvent the residue was recrystallised from alcohol whereby 8-methyl-7-hydroxy coumarin was obtained melting at 231–32°. A mixture of this specimen with the one made from 2-methyl-resorcinol melted at the same temperature [Found C, 72.5, H, 4.5, $C_{10}H_8O_3$ requires C, 72.7, H, 4.6%]

7-Methoxy-8-methyl-coumarin (IX)—The above hydroxy coumarin (1 g) was dissolved in anhydrous acetone (20 c.c.), excess of methyl iodide (2 c.c.) and potassium carbonate (2 g) added and the mixture gently boiled under reflux for 20 hours. After filtering, the clear solution was distilled in order to recover the solvent, the solid residue was taken up in ether and washed with dilute sodium hydroxide in order to remove unmethylated hydroxy compound. After final washing with water, it was evaporated and the residue crystallised from alcohol. Colourless rectangular prisms and plates melting at 122–23° were obtained. This sample was found to be identical with the one prepared from the nuclear methylation product of β -resorcylic aldehyde [Found C, 69.4, H, 5.6, $C_{11}H_{10}O_3$ requires C, 69.5, H, 5.3%]

Summary

A survey of past work on the nuclear methylation and ethylation of resorcinol and phloroglucinol derivatives is given and a mechanism for this reaction suggested. The nuclear methylation of β -resorcylic aldehyde has now been carried out giving rise to a good yield of the product (A). Its constitution as 4-methoxy-3-methyl-2-hydroxy benzaldehyde has been established in two ways: (i) A sample of 4-methoxy-3-methyl-2-hydroxy benzaldehyde was prepared according to the synthetic method of Jones and Robertson and compared with (A). (ii) The corresponding coumarin was prepared from (A) and was identified as 7-methoxy-8-methyl coumarin by comparison with the compound obtained by independent synthesis, starting from 2-methyl-resorcinol and passing through 7-hydroxy-8-methyl-coumarin as an intermediate stage. The same coumarin was also prepared by the reduction of umbelliferone-8-aldehyde and subsequent methylation.

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THE CONSTITUTIONAL FEATURES OF ANTHOXANTHINS IN RELATION TO THE MORIN REACTION IN ANALYTICAL CHEMISTRY

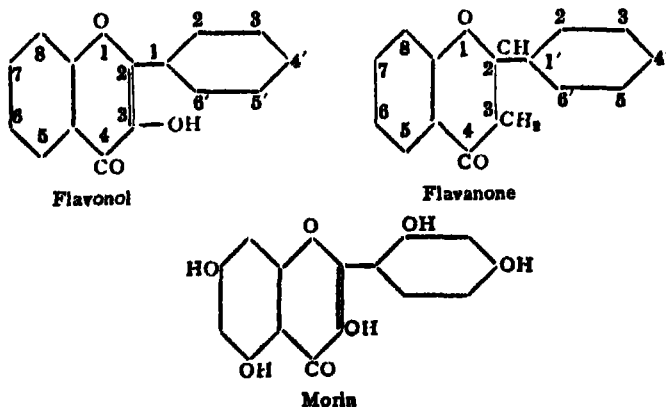
Part I. Some Naturally Occurring Hydroxy-flavonols and Flavanones

BY K. NEELAKANTAM AND L. RAMACHANDRA ROW

(From the Department of Chemistry, Andhra University, Waltair)

Received August 5, 1941

MORIN (5, 7, 2', 4'-tetrahydroxyflavonol) was first introduced by Goppelsroeder¹ in 1868 as a reagent for the detection of small amounts of aluminium with which it yields in weakly acid solutions, a very prominent green or blue-green fluorescence ordinarily visible in daylight. This reaction did not receive much attention until Schantl² in 1924 showed that it is a very sensitive reaction, as little as 10^{-8} mg. of the element in 10 c.c. of the solution being detected with the aid of Tswett's luminoscope. Since then it has received considerable attention, as a result of which it is now known not to be specific for aluminium. A similar yellowish green fluorescence has also been obtained with beryllium,³ and a large number of other metals, and the acid radicals, arsenite and arsenate.^{3, 4, 5} In spite of this defect, this reaction has been utilised for the detection, as well as determination of aluminium and beryllium, and the fluoride ion indirectly.^{3, 6, 7} However, no attempt has been made till now to study the influence of constitutional factors in morin over the appearance of fluorescence with aluminium or any of the other metals.



The correlation of constitution with fluorescence is a problem of considerable difficulty. In the group of hydroxyflavonols of which morin is one, a considerable amount of investigation has been done regarding the relation between number and position of hydroxyls and the tinctorial properties of these compounds,¹⁰ but not much work has yet been done regarding the fluorescence which some of them exhibit under certain conditions. It is only recently that Rangaswami and Seshadri¹¹ examined this problem with reference to the closely allied hydroxy-flavones.

Several of the naturally occurring as well as the synthetic flavonols exhibit fluorescence in daylight, when dissolved in concentrated sulphuric acid, and a few in alkaline solution. Fisetin and the isomeric 6, 3', 4'-trihydroxy-flavonol are exceptional in that they exhibit fluorescence in alcoholic solutions. Morin itself yields a bluish green fluorescence in concentrated sulphuric acid, but none in alkaline solutions. It is, however, a unique case of a hydroxy-flavonol which yields fluorescence with metals in alkaline or acid solutions and so far employed in analytical chemistry. As is well known, the hydroxy-flavonols have marked dyeing properties and yield coloured lakes with metals such as aluminium, beryllium, etc. Morin behaves similarly but surprisingly enough it yields with the same metals in dilute solutions very prominent fluorescence in daylight itself. This fluorescence has been ascribed to a neutral, colloiddally dispersed aluminium salt of morin having the formula $\text{Al}(\text{C}_{15}\text{H}_9\text{O}_7)_3$,² but it seems probable that the paraquinonoid structure which these lakes possess¹⁰ also plays an important part. The fact that a wide variety of metals yields similar fluorescence seems to support this view.

As a result of the investigations on the anthoxanthin pigments of flowers which have been in progress in these laboratories for several years, a number of compounds which have certain similarities and certain differences when compared with morin were available and, therefore, it was considered desirable to examine them in order to throw more light on the problem of the fluorescence obtained in the morin reactions. The examination was, however, limited to the reaction of morin with aluminium and beryllium as in practice this reaction is mostly used for the detection and determination of these metals.

Experimental

For the following experiments pure samples of the flavanones, naringenin, butin and hesperitin, and the flavonols, kempferol, quercetin, herbacetin, gossypetin and quercetagenin which were obtained from natural sources were used.

Preparation of Solutions

Reagents—Saturated solutions of all the pigments, except k mpferol and herbacetin, in methyl alcohol were employed. The available amount of k mpferol and herbacetin being small only dilute solutions were used.

Test Solutions (1) *Aluminium*—A dilute solution of potash alum was prepared using A R quality sample and standardised by precipitating the aluminium with 8-oxyquinoline. It was then diluted to contain 1 mg of aluminium per c c.

(2) *Beryllium*—A dilute solution of beryllium nitrate was prepared using a "Pure" sample and the absence of aluminium was assured by testing with "Oxine". It was standardised by precipitating the beryllium as hydroxide and igniting to the oxide, and then diluted to contain 1 mg. of beryllium per c c.

(3) *Potash*—A dilute (2 N) solution of potassium hydroxide was prepared and tested for the absence of aluminium by the "Oxine" method.

Procedure—Tests were carried out in alkaline, as well as in solutions acidified with acetic acid, with aluminium and beryllium provided the reagent itself did not undergo atmospheric oxidation in alkaline solution.

One c c of the test solution was placed in a quartz test-tube and treated with dilute potash until precipitation occurred. Thereafter, the precipitate was either dissolved in acetic acid or in an excess of the alkali, the solution diluted to 10 c c with water and treated with one or more drops of the reagent. Observations were made first in daylight and then under the "Cenco Black Light Source" which consists of an argon-mixed gas glow lamp provided with a U V filter which allowed light down to 3100 Å to pass through.

Results

Blank tests were carried out in all cases on the reagents themselves under identical conditions; the results were negative in all except hesperitin, 4'-methoxy-3' 5 7-trihydroxyflavanone (*Citrus aurantium* peels) which gave in alkaline solution under the lamp a bright blue fluorescence which was destroyed by acetic acid. Similar results were obtained with hesperitin in alkaline as well as in acetic acid solutions both with aluminium and beryllium. For comparison the reactions were carried out with a saturated solution of morin in methyl alcohol. With the reagents recorded in the table below, however, no fluorescence was observed in daylight and in no case was it so very prominent as with morin under identical conditions. The results obtained under the lamp are recorded in a tabular form below:

Reagent	Sources	Aluminium	Beryllium	Remarks
1 Naringenin (5 7 4'-trihydroxy-flavanone)	Flowers of <i>Citrus decumana</i>	Faint bluish fluorescence in acetic acid, alkaline solution yellow in colour but no fluorescence	Faint bluish fluorescence in acetic acid, alkaline solution deep yellow with a bluish fluorescence	
2 Kämpferol (5 7 4'-trihydroxy-flavonol)	Senna leaves	Alkaline solution yellow in colour with no fluorescence. In faintly alkaline or almost neutral solution, a bluish green fluorescence, moderately strong, on adding acetic acid the fluorescence is practically unchanged	Bright yellow solution in alkalies with a bright greenish yellow fluorescence. None in acetic acid	
3 Herbacetin (5 7 8 4'-tetrahydroxy flavonol)	Flowers of <i>Gossypium herbaceum</i>	Bright yellow solution with no fluorescence in acetic acid	Bright yellow solution with no fluorescence in acetic acid	The reagent undergoes oxidation in alkaline solutions
4 Morin (5 7 2' 4'-tetrahydroxy-flavonol)	Schering-Kahlbaum, Berlin	In acetic acid extraordinarily brilliant green fluorescence, in alkaline solutions deep yellow without any fluorescence	In acetic acid no fluorescence, in alkaline solution chromate yellow with deep yellowish green fluorescence	Identical results were obtained even in daylight in both cases
5 Quercetin. (5 7 3 4'-tetrahydroxy-flavonol)	Flowers of <i>Gossypium herbaceum</i>	Bright yellow solution with yellowish green fluorescence in acetic acid, deep yellow solution with no fluorescence in alkalies	Bright yellow solution with no fluorescence in acetic acid, deep yellow solution with a very feeble greenish fluorescence in alkalies	
6 Gossypetin (5 7 8 3' 4'-pentahydroxy-flavonol)	Do	Yellow solution with no fluorescence in acetic acid.	Pale yellow solution with no fluorescence in acetic acid	Undergoes oxidation in alkaline solutions
7 Quercetagenin. (5 6 7 3 4'-pentahydroxy-flavonol)	Flowers of <i>Tagetes erecta</i>	Yellow solution with no fluorescence in acetic acid	Yellow solution without any fluorescence in acetic acid	Undergoes oxidation in alkaline solutions.
8 Butin (7 3' 4'-trihydroxy-flavanone)	Flowers of <i>Butea frondosa</i>	In acetic acid solution pale yellow with no fluorescence; in alkaline solution, only red with no fluorescence	In acetic acid pale yellow solution with no fluorescence; in alkalies a red solution with no fluorescence.	In alkaline solution the compound is converted rapidly into the corresponding chalcone butein.

Discussion

The results obtained show that among the group of compounds examined morin is exceptional in giving a very prominent fluorescence, none of the others gives any fluorescence with aluminium or beryllium in daylight and the fluorescence observed under the lamp is not at all so intense. A comparison of these results, however, throws light on the relation between the constitution of these compounds and the fluorescence. The only difference between morin and quercetin is in the 2'- instead of 3'- position of one hydroxyl in the side phenyl group and the difference in behaviour may, therefore, be due to the 2'-position of one hydroxyl. The results obtained with k mpferol and morin show the intensifying effect of a hydroxyl in the 2'-position on the fluorescence given by a 4'-hydroxy compound. A comparison of k mpferol with herbacetin reveals the inhibitory effect of the 8-hydroxyl. This conclusion is further supported by the comparison of quercetin with gossypetin. Further the available data shows the inhibitory effect of 6-hydroxyl as in quercetagenin. The exhibition of fluorescence both by k mpferol and naringenin shows that the 3-hydroxyl is not absolutely necessary for the appearance of fluorescence with metals. It thus appears probable that a hydroxyl in 2'-position alone or in conjunction with a 4'-hydroxyl is responsible for the brilliant fluorescence obtained with morin and metals. This conclusion seems to be supported by the fact that morin unlike other flavonols, yields an anhydrosulphate ($C_{15}H_8O_6$, H_2SO_4) when treated with concentrated sulphuric acid, and this behaviour is closely related to the presence of a hydroxyl in the 2'-position.¹² If this conclusion were correct, similarly constituted compounds such as datiscetin (5, 7, 2'-trihydroxyflavonol), resomorin (7, 2', 4'-trihydroxyflavonol), and 5, 7, 2', 4'-tetrahydroxyflavone synthesised by Robinson and Venkata Raman,¹² should yield similar results with metals. Further work is in progress along these lines.

The authors wish to thank Prof. T. R. Seshadri for help and encouragement during the course of this investigation.

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A RELATION BETWEEN A PENCIL AND A RANGE OF QUADRICS*

BY SAHIB RAM MANDAN

(The University of the Punjab, Lahore)

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THE purpose of this paper is to establish a relation between a pencil and a range of quadrics and thence deduce the equivalence of two symmetrical determinants differing in order by unity

1 We start with the quadrics $\Sigma, \Sigma_1, (i = 1, 2)$ of a pencil. Let C, C' be the enveloping cones of Σ and Σ_1 having their vertices at the poles P, P' of a plane Π w r t Σ and Σ_1 respectively, i.e., the cones and the quadrics have the same plane of contact Π . Now if Σ_2 pass through the twisted quartic common to C and C' , P' will lie on the quadric Σ_1' reciprocal of Σ w r t. a quadric Σ_{12} for which Σ_1 and Σ_2 are reciprocal. We thus arrive at the quadrics Σ', Σ , of a range

As P, P' are the vertices of two cones of the pencil of quadrics of which Σ_2 is a member, the polar plane Π of P w r t Σ_2 passes through P' and is the polar plane of the line PP' w r t C' . The pole of Π w r t Σ_1 is therefore conjugate to P w r t Σ and in such a case it can be proved that Π touches Σ' . Now the poles of a plane w r t. a range of quadrics lie on a line, the point of contact of Π with Σ' is therefore found to be P' , i.e., P' lies on Σ' .

2 Let the point-equations of Σ , be $S_1(x, y, z, t) = a_1x^2 + 2f_1yz + \dots + 2u_1xt + \dots = 0$ and their tangential equations be $\Sigma_1(l, m, n, p) = A_1l^2 + \dots + 2F_1mn + \dots + 2U_1lt + \dots = 0$ with usual notations for $A_1, \dots, F_1, \dots, U_1, \dots$.

Consider the equation $Q = \lambda S_2(x, y, z, t) + S_1(x, y, z, t) \cdot S_1 - \Pi'^2 = 0$ where S_i stands for $S_i(a, \beta, \gamma, \delta)$; $\Pi' = xS_{1\alpha} + yS_{1\beta} + zS_{1\gamma} + tS_{1\delta}$, $2S_{1\alpha} = \frac{\partial S_1}{\partial a}$, $2S_{1\beta} = \frac{\partial S_1}{\partial \beta}$, $\dots, S_1, \lambda \neq 0$. Now $S_1(x, y, z) \cdot S_1 - \Pi'^2 = 0$ represents an enveloping cone C' of Σ_1 having its vertex at $P'(a, \beta, \gamma, \delta)$. Suppose the

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quadric $Q=0$ to be a cone C , its discriminant then must vanish, i.e., $\alpha, \beta, \gamma, \delta$ should satisfy the condition given by the equation $D_1'=0$

where

$$D_1' = \begin{vmatrix} \lambda a_2 + a_1 S_1 - S_{1\alpha}^2, & \lambda h_2 + h_1 S_1 - S_{1\alpha} S_{1\beta}, & \lambda g_2 + g_1 S_1 - S_{1\alpha} S_{1\gamma}, & \lambda u_2 + u_1 S_1 - S_{1\alpha} S_{1\delta} \\ & \lambda b_2 + b_1 S_1 - S_{1\beta}^2, & \lambda f_2 + f_1 S_1 - S_{1\beta} S_{1\gamma}, & \lambda v_2 + v_1 S_1 - S_{1\beta} S_{1\delta} \\ & & \lambda C_2 + C_1 S_1 - S_{1\gamma}^2, & \lambda w_2 + w_1 S_1 - S_{1\gamma} S_{1\delta} \\ & & & \lambda a_2 + a_1 S_1 - S_{1\delta}^2 \end{vmatrix}$$

Again taking the quadric Σ as $\lambda S_2(\lambda, y, z, t) + S_1(\lambda, y, z, t) S_1 = 0$ and the plane Π' as $\Pi' = 0$, we find that the cones C, C' satisfy the conditions imposed upon them in §1. Therefore, P' lies on the quadric Σ' whose tangential equation will be $\lambda \frac{\Sigma_1(l, m, n, p)}{\Delta_1} + \frac{\Sigma_2(l, m, n, p)}{\Delta_2} S_1 = 0$ where Δ_i ($\neq 0$) is the discriminant of the quadric $S_i(x, y, z, t) = 0$, i.e., $\alpha, \beta, \gamma, \delta$ should satisfy the equation $D_2' = 0$ where

$$D_2' = \begin{vmatrix} \lambda A_1 + \frac{A_2}{\Delta_2} S_1, & \frac{\lambda H_1}{\Delta_1} + \frac{H_2}{\Delta_2} S_1, & \frac{\lambda G_1}{\Delta_1} + \frac{G_2}{\Delta_2} S_1, & \frac{\lambda U_1}{\Delta_1} + \frac{U_2}{\Delta_2} S_1, & \alpha \\ & \frac{\lambda B_1}{\Delta_1} + \frac{B_2}{\Delta_2} S_1, & & & \beta \\ & & & & \gamma \\ & & & & \delta \\ & & & & 0 \end{vmatrix}$$

The two determinantal equations $D_1' = 0$ arise from the same proposition looked from two different angles. Hence they must be equivalent, i.e., $D_1' = KD_2'$. This equality can be otherwise* proved immediately and directly if D_1' be written in the following form (ignoring a multiplicative constant).

$$\begin{vmatrix} \frac{\lambda a_2}{S_1} + a_1, & \dots & \dots & \dots & S_{1\alpha} \\ & \frac{\lambda b_2}{S_1} + b_1, & \dots & \dots & S_{1\beta} \\ & & \dots & \dots & S_{1\gamma} \\ & & & \dots & S_{1\delta} \\ S_{2\alpha}, & S_{2\beta}, & S_{2\gamma}, & S_{2\delta}, & 0 \end{vmatrix}$$

and writing $\lambda = \mu S_1$, it assumes a good symmetric form in both S_1 and S_2 .

* Suggested by the referee.

3 Further, let Σ_i be the quadrics as in §2 and consider the quadric $Q = \lambda S_2(x, y, z, t) + C' = 0$ where $C' = \psi_\alpha^2 S_1(x, y, z, t) + \psi_x(\psi_x S_1 - 2\psi_\alpha \Pi')$ S_1, Π' being as in §2, $\psi_x = ax + by + cz + dt$, $\psi_\alpha = a\alpha + b\beta + c\gamma + d\delta (\neq 0)$ Now if we call the conic $S_1(x, y, z, t) = 0 = \psi_x$ as σ_1 , $C' = 0$ will represent the cone C' passing through σ_1 with its vertex at $P'(a, \beta, \gamma, \delta)$ Suppose the quadric Q to be a cone, then its discriminant must vanish, i.e., a, β, γ, δ should satisfy the condition expressed by the equation $D_1' = 0$ where $D_1' =$

$$\left| \begin{array}{cccc} \lambda a_2 + \psi_\alpha^2 a_1 + a^2 S_1 & \lambda h_2 + \psi_\alpha^2 h_1 + ab S_1 & \lambda g_2 + \psi_\alpha^2 g_1 + ca S_1 & \lambda u_2 + \psi_\alpha^2 u_1 + ad S_1 \\ -2a\psi_\alpha S_{1\alpha} & -\psi_\alpha (aS_{1\beta} + bS_{1\alpha}) & -\psi_\alpha (cS_{1\alpha} + aS_{1\gamma}) & -\psi_\alpha (aS_{1\delta} + S_{1\alpha}) \\ \lambda b_2 + \psi_\alpha^2 b_1 + b^2 S_1 & & & \\ & -2b\psi_\alpha S_{1\beta} & & \end{array} \right|$$

Again let $V(A, B, C, D)$ be the pole of the plane $\psi_x = 0$ w.r.t. Σ_2 and $S_2(V) = S_2(A, B, C, D)$, $2S_{2A} = \frac{\partial S_2(V)}{\partial A}$, $\psi_A = aA + bB + cC + dD$, $C_1' = S_1(x, y, z, t) + \frac{\psi_x}{\psi_A^2} [\psi_x S_1(V) - 2\psi_A (\lambda S_{1A} +$
 $+)]$, $C_2' = S_2(x, y, z, t) - \frac{\psi_x^2}{S_2(V)}$, $\Sigma_1' = C_1' + \lambda \frac{\psi_x^2}{\psi_A^2 S_2(V)}$, $\Sigma = \lambda C_2' + \psi_\alpha^2 \Sigma_1'$, then $Q = \Sigma + \psi_x \psi_x'$ where $\psi_x' = \psi_x \left[(S_1 - S_1(V) \left(\frac{\psi_\alpha}{\psi_A} \right)^2 \right]$
 $- 2\psi_\alpha [xS_{1\alpha} + \dots - \frac{\psi_\alpha}{\psi_A} (xS_{1\alpha} + \dots +)]$

Let ψ, ψ' be the planes $\psi_x = 0$ and $\psi_x' = 0$, μ be their common line; P be the vertex of the cone Q and Π'' be the polar plane of P w.r.t. the quadric $\Sigma = 0$ Now it is easy to see that the planes $P\mu$ and $V\mu$ are harmonically conjugate w.r.t. the planes ψ and $\psi_x' + \frac{\lambda\psi_x}{S_2(V)} = 0$, and the planes ψ, ψ' are separated harmonically by the pairs of planes $P'\mu, V\mu, \Pi'', P\mu$; $\psi_x' + \frac{\lambda\psi_x}{S_2(V)} = 0, \psi_x' - \frac{\lambda\psi_x}{S_2(V)} = 0$ as $Q = \lambda C_2' + \psi_\alpha^2 C_1' + \psi_x \left(\psi_x' + \frac{\lambda\psi_x}{S_2(V)} \right)$
 $= \Sigma + \psi_x \psi_x'$ and $C' = C_1' \psi_\alpha^2 + \psi_x \psi_x'$ From these results and that $C' = \psi_\alpha^2 \Sigma_1' + \psi_x \left(\psi_x' - \frac{\lambda\psi_x}{S_2(V)} \right)$ it follows that the polar plane of P' w.r.t. the quadric $\Sigma_1' = 0$ is Π'' as the harmonic conjugate of the plane $P'\mu$ w.r.t. ψ and $\psi_x' - \frac{\lambda\psi_x}{S_2(V)} = 0$.

Now the quadric Σ_2 and the cones Q, C' belong to a pencil, therefore the polar plane Π of P w r t Σ_2 passes through P' and is the polar plane of the line PP' w r t C' . The pole of the plane Π w r t $\Sigma_1' = 0$ is hence conjugate to P and in such a case it can be proved that Π touches the quadric Σ' , reciprocal of $\Sigma = 0$ w r t a quadric Σ_{12}' for which $\Sigma_1' = 0$ and Σ_2 are reciprocal

Again the quadrics $\Sigma = 0, \Sigma_1' = 0$ and the cone C_2' belong to a pencil, C_2' being the enveloping cone of Σ_2 with its vertex at V , reciprocates into the conic σ_1 w r t $\Sigma_{12}', \Sigma', \Sigma_2, \sigma_1$ therefore belong to a range. The pole of the plane Π w r t σ_1 being the point where the line PP' meets ψ , the point of its contact with Σ' will be no other than the point P' . Hence P' lies on Σ' whose tangential equation will be

$$\lambda [\Sigma_1(l, m, n, p) - \Sigma_1 - (l\Sigma_{1a} + m\Sigma_{1b} + \dots + \dots)^2] + \psi_a^2 \Sigma_2(l, m, n, p) = 0$$

where $\Sigma_i = \Sigma_i(a, b, c, d) (\neq 0)$, $2\Sigma_{ia} = \frac{\partial \Sigma_i}{\partial a}$, \dots , $i.e., \alpha, \beta, \gamma, \delta$

should satisfy the condition expressed by the equation $D_2' = 0$ where $D_2' =$

$$\left| \begin{array}{cccc} \frac{\lambda}{\Delta_1 \Sigma_1} (A_1 \Sigma_1 - \Sigma_{1a}^2) & \frac{\lambda}{\Delta_1 \Sigma_1} (H_1 \Sigma_1 - \Sigma_{1a} \Sigma_{1b}) + \psi_a^2 \frac{H_2}{\Delta_2} & \frac{\lambda}{\Delta_1 \Sigma_1} (G_1 \Sigma_1 - \Sigma_{1a} \Sigma_{1c}) & , \alpha \\ + \psi_a^2 \frac{A_2}{\Delta_2} & & + \psi_a^2 \frac{G_2}{\Delta_2} & \\ \frac{\lambda}{\Delta_1 \Sigma_1} (B_1 \Sigma_1 - \Sigma_{1b}^2) + \psi_a^2 \frac{B_2}{\Delta_2} & , & & \beta \\ , & , & , & \gamma \\ , & , & \dots & \delta \\ & & & 0 \end{array} \right|$$

The two determinantal equations $D_1' = 0$ arise from the same proposition looked from two different points of view. Hence they must be equivalent, i.e., $D_1' = K D_2'^*$

4 It may be remarked here that if the quadric Q of §3 break into a pair of planes, $\Sigma = 0$ must degenerate into a cone with its vertex on the line μ and thence Σ' degenerates into a conic. From this result and the preceding one we can derive certain properties of the focal conics of a confocal system by taking σ_1 as the circle at infinity.

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* A similar analysis can be applied for this equality also to prove it directly and immediately as in §2

THE QUANTUM THEORY OF X-RAY REFLECTION: BASIC IDEAS

BY SIR C V RAMAN, KT, FRS, NL

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE phenomena arising when a beam of X-rays traverses a crystal and ascribable to the possible or actual movements of the atoms in it from their positions of equilibrium are of very great interest, since their study may be expected to throw light on the nature of such atomic movements and also on the nature of the interaction between the X-rays and the material particles of the medium. In the analogous case of a beam of monochromatic light traversing a transparent crystal, the phenomenon of the scattering of light with change of frequency first observed by the present writer in 1928 renders a direct spectroscopic investigation of the atomic vibrations possible. Much light has been recently thrown on the subject of crystal physics by such spectroscopic studies. Indeed, the new knowledge derived in this way necessitates a radical revision of the ideas hitherto accepted concerning the dynamics of crystal lattices and the thermal energy of crystals. Further, the optical investigations show very clearly that the interchanges of energy and momentum between the radiation and the crystal lattice are determined by the principles of the quantum mechanics and not by the

classical ideas Early last year (1940), it was observed by Dr P Nilakantan and the present writer that the (111) crystal planes of diamond exhibit monochromatic X-ray reflections of a new type which are as sharply defined as the ordinary or Laue reflections but which obey a wholly different geometric law Further, the intensity of these reflections, though definitely smaller than the intensity of the classical X-ray reflections, is of the same order of magnitude and is not appreciably altered by either rise or fall of the temperature of the crystal These and other observations of a fundamental character revealed the existence of a whole group of X-ray phenomena which lie outside the scope of the existing theoretical developments of the subject It thus becomes necessary to re-examine the assumptions on which the existing theories are based and to build a new theoretical structure in better accord with facts

2 *The Failure of the Classical Mechanics*

In an essay on the molecular diffraction of light published in 1922, the present writer showed that, contrary to the opinion generally held at that time, transparent crystals such as quartz, rock-salt and ice traversed by a beam of light exhibit a true opalescence or diffusion of light associated with the ultimate structure of the crystal This diffusion was provisionally attributed to the disordering of the crystal lattice by thermal agitation The subsequent observation by the present writer that the spectrum of the light so scattered by crystals exhibits changes of frequency placed a new complexion on the matter The incident light being monochromatic, frequency differences between the incident and scattered radiations are observed which fall in the infra-red region of the spectrum and are therefore to be identified with certain specific modes of vibration of the crystal structure If the appearance of such vibrations in the spectrum of the scattered light had been due to thermal agitation in the crystal, it would follow from the principles of optics and electrodynamics that the radiations of *increased* and *diminished* frequencies should appear with *equal intensity* Actually, this is very far from being the case Indeed, when the frequency differences are large, we observe *only* scattered radiations with diminished and *none* of increased frequencies These facts indicate that the vibrations of the crystal lattice revealed by the spectroscope are produced or induced by the light itself Further, quantitative studies of intensity show that this is the correct view of the matter even if such vibrations are of sufficiently low frequency to be appreciably excited by thermal agitation The light induces a step-down or a further step-up of the vibration as the case may be, appearing as scattered light with increased

and diminished frequencies respectively, though with greater intensity corresponding to the greater amplitude of vibration. The facts thus compel us to recognise that the observed scattering of light is in every case associated with the changes in the energy level of vibration induced by the light itself.

The spectroscopic evidence thus makes it clear that the scattering of light in crystals is a quantum-mechanical effect, the exchanges of energy between the photons and the crystal lattice occurring in discrete units or quanta of vibrational energy. When these units of energy are sufficiently small, in other words when the frequencies of mechanical vibration of the crystal lattice are sufficiently low, the quantum-mechanical picture of the facts tends asymptotically towards the purely classical picture in which the scattered light should appear with equal intensity with increased and diminished frequencies. In other words, the quantum description has a classical analogue, the latter, however, bears no resemblance to the facts except when the vibrations of the crystal are of very low frequency or the temperature of the crystal is very high. The lower the temperature of the crystal, and the higher the frequency of a particular vibration, the less would the actual facts resemble the picture suggested by the classical ideas.

That the propagation of X-rays through a crystal is influenced by the atomic vibrations is shown by the diminishing intensity of the spots in a Laue pattern when the crystal is heated. Numerous physicists, amongst them Debye (1914), Brillouin (1922), Waller (1923, 1927), and Laue (1926), have considered this problem from a semi-classical point of view. Laue in his memoir of 1926 drew attention to a very important feature emerging from his treatment of the problem, namely that all secondary radiations from the crystal, except those appearing as the geometric reflections by the lattice planes, suffer a change of frequency. The origin of this change of frequency is readily understood. An atom occupying a fixed position in space would naturally emit secondary radiations having the same frequency as the primary X-ray falling upon it. An oscillation of the atom about its position of equilibrium would result in a periodic variation of phase of such secondary radiation. The analysis indicates that the secondary radiations would then include components with their frequency increased and diminished respectively by the oscillation frequency of the atom. These components appear with an intensity which rapidly increases with the amplitude of the atomic vibration, the intensity of the component of unmodified frequency diminishing *pari passu*. Laue emphasised that these changes of frequency play a fundamental rôle in determining the observed optical effects. For, only such radiations as have identically the same

frequency can be coherent with each other, any difference of frequency however small would render coherence impossible. A frequency analysis of the secondary radiations and therefore also of the atomic vibrations is thus a necessary preliminary to a proper investigation of the problem.

Laue showed that the secondary radiations from the atoms in the crystal vibrating with a specified frequency yield a resultant in which the *components with increased and diminished frequency appear superposed with identical intensity*. The situation is thus exactly similar to that arising in the theory of the scattering of light in a crystal when considered classically, and it automatically follows that the classical mechanics must also fail in the X-ray problem. The change over from classical to quantum mechanics is fortunately simple. The conservation of energy as between the X-ray quantum and the crystal is equivalent classically to a change of frequency of the radiation, such change, however, occurring in one direction or the other and not in both at once. The conservation of momentum in the encounter between the X-ray quantum and the crystal is equivalent classically to the usual formula for a monochromatic reflection of incident radiation by a stratified medium, the stratifications being now dynamic and not static. The correct intensity for the radiation of modified frequency resulting from the encounter is found by associating one energy quantum of the appropriate frequency with each degree of freedom of vibration of the crystal lattice. The effect of thermal agitation in the crystal enters into the quantum mechanical scheme for the X-ray problem in exactly the same way as in the parallel problem of the scattering of light.

3 *The Vibration Spectrum of a Crystal*

Einstein who was the pioneer in the development of the quantum theory of specific heats suggested that the vibrations of the atoms in a solid have *monochromatic* frequencies and showed how these frequencies could be connected with the observed variation of specific heat with temperature. He also explained how in simple cases the order of magnitude of these frequencies could be inferred from the elastic properties of the solid. The alternative hypothesis put forward by Debye, namely that the frequencies of atomic vibration in a solid form a continuous spectrum which may be identified with its elastic vibrations, subsequently however found its way into general favour. The success of the Debye formula in representing the course of the specific heat curve in several cases promoted the belief that the hypothesis correctly represents the actual vibration spectrum of simple solids. That this belief is illusory becomes evident on a closer examination of the facts.

In the first place, it may be pointed out that while a knowledge of the vibration spectrum enables us uniquely to determine the specific heat curve, it can scarcely be suggested that a knowledge of the specific heat curve enables us uniquely to determine the vibration spectrum. Indeed, whenever it has been possible to make a direct spectroscopic study of the vibration spectrum of a solid, the claim of the Debye hypothesis to represent the same is shown to be false. Taking for instance the case of diamond, the studies of Bhagavantam (1930) on the scattering of light in this crystal, and the recent investigations of Nayar (1941) on its luminescence at low temperatures show the lattice spectrum of diamond to consist of numerous discrete or monochromatic frequencies, some of them being much smaller than the so-called limiting frequency calculated from the Debye formula. The spectrum of the scattering of light in sulphur and phosphorus similarly exhibits numerous discrete lines, including some with very low frequency shifts, indicating that most of the degrees of freedom of atomic vibration are represented by monochromatic vibrations as originally pictured by Einstein. The position is equally striking when we consider crystals of apparently simple chemical composition, *e.g.*, quartz. Mr Saksena (1940) has shown by a detailed investigation that no less than 24 out of every 27 degrees of freedom are represented in the vibration spectrum of this crystal by monochromatic frequencies.

It is known that the Debye formula fails to represent the specific heat curves correctly in several cases. It may be pointed out that these failures are actually more significant than the successes of the formula in other cases. Elaborate hypothesis have been put forward to explain away these failures, overlooking the simple explanation indicated by the spectroscope, namely, that the vibration spectrum of every crystal, however simple in its chemical composition, includes several monochromatic frequencies. When these frequencies are known, the specific heat formula necessarily contains corresponding Einstein terms, and this involves a reduction (usually very drastic) in the number of degrees of freedom allotted to the Debye term, as also of its "limiting frequency". In the case of diamond, for example, it is shown in a forthcoming paper by Mr V B Anand that the specific heat data are perfectly expressed in this way by the spectroscopically observed frequencies, only one-eighth of the total number of degrees of freedom being included in a term of the Debye type. On the other hand, a Debye function alone even with an arbitrarily assumed "limiting frequency" shows large deviations from the observed specific heats. It may reasonably be inferred that in other cases, *e.g.*, metallic silicon or grey tin, where the Debye formula altogether fails to represent the specific heat data, the cause of failure is the same,

namely that the vibration spectrum includes several monochromatic frequencies.

Thus, both the spectroscopic and specific heat data show unmistakably that the Debye picture of the vibration spectrum of a solid bears no resemblance to the facts, except in the region where it is *prima facie* appropriate, namely in respect of the elastic solid vibrations of the lowest frequencies whose wave-length is large compared with the lattice spacings of the crystal. The maximum possible contribution which such vibrations can make to the specific heat of the solid can be found by treating the lattice cell in the crystal as a single unit and assigning it three degrees of freedom of translatory movement. All other degrees of freedom of movement are necessarily associated with monochromatic or Einstein frequencies of vibration of the crystal structure. Thus, in all crystals, including even those which are elementary or of the simplest chemical composition, the vibration spectrum is essentially of the type pictured by Einstein, and consists of discrete or monochromatic frequencies lying in the infra-red or high-frequency region. This is accompanied in the region of low frequencies by a continuous spectrum of elastic vibrations. The contribution of the latter to the thermal energy would be relatively of minor importance for the vast majority of crystals except at the lowest temperatures.

4 Character of the Einstein Vibrations

We may now proceed to consider the nature of the monochromatic vibrations. It is evident that they arise from a periodic variation with time of the basic grouping of the atoms in the unit cells of the lattice. Such a vibration obviously cannot be confined to an individual cell, for its energy would then be rapidly passed on to the neighbouring cells and would be immediately damped out. We must, in fact, picture the vibrations as taking place simultaneously and in identically the same way in all the cells of the lattice. The frequency of such vibrations as well as their modes would be determined by the internal architecture of the crystal, in other words by the geometric grouping of the atoms and the forces which they exert on each other. If the number of the lattice cells be sufficiently large, as would be the case even for a sub-microscopic crystal, these frequencies and modes would be wholly independent of the size or shape of the crystal. The vibrations must, in the limiting case, be pictured as having an identical frequency, amplitude, and phase in all the cells of the lattice, as only then could the motion be truly monochromatic. Any variation in the phase of the vibration at different points in the crystal would involve a departure from perfect monochromatism, but this would be negligible provided the

phase wave-length is sufficiently great to include a large number of lattice cells. Phase wave-lengths comparable with the dimensions of the lattice cells would be altogether excluded, and in general the smaller wave-lengths would be much less probable than the larger ones for which the frequency is independent of wave-length. The possible orientations of the phase waves would be determined by the geometry of the atomic grouping and especially by its symmetry characters.

Turning now to the continuous spectrum of elastic or low frequency vibrations, the situation here is totally different. The atomic structure of the solid does not enter into the picture. The possible frequencies of vibration are explicitly determined by the macroscopic dimensions of the crystal and their relation to the velocity of the wave propagation, the spectrum extending continually towards lower frequencies as the dimensions of the crystal are enlarged. The frequencies vary with the wave-lengths, being inversely proportional to them. The possible wave-lengths being determined by the dimensions of the crystal, it follows from simple geometry that the cases in which the wave-lengths are small are much more numerous than those in which they are large. Further, the orientation of the wave-fronts is entirely arbitrary and bears no relation whatsoever to the symmetry characters of the crystal or its atomic architecture.

5 *The Fallacy of the Born Postulate*

As shown in the preceding pages, facts and principles alike compel us to reject the hypothesis of Debye as a description of the vibration spectrum of a crystalline solid except in the restricted region of low frequencies. We have also seen that these low-frequency vibrations are altogether different in their character from the vibrations of higher frequency lying in the infra-red region of the spectrum. It follows that any treatment of the problems of crystal dynamics based on the concepts of Debye is necessarily fallacious. It may be remarked that the basic idea underlying Max Born's crystal dynamics is essentially the same as that of Debye, namely that all the possible vibrations of a crystal lattice are analogous to the elastic vibrations, having the same distribution of the phase-waves in respect of the wave-lengths and their relation to the size of the crystal, as well as an identically similar distribution of the phase waves in respect of orientation in space. No proof or justification of this postulate seems ever to have been put forward. The so-called postulate of the "cyclic lattice" is in fact nothing more than an *ad hoc* hypothesis adopted for mathematical convenience. It is evident that this postulate is in total conflict with the conclusions at which we have arrived regarding the characters of the mono-

chromatic vibrations of the crystal lattice We shall therefore proceed to examine the Born postulate critically with reference to its claims to represent the actual state of affairs in a crystal

One of the most remarkable facts brought into evidence by the study of the scattering of light in crystals is the extreme sharpness of the lines observed in the spectra of such scattering Even in those few cases where the spectrum exhibits bands having an observable breadth, these sharpen to the finest lines when the crystal is cooled down to low temperatures A perfect monochromatism of the vibrations of the lattice in the infra-red region is thus to be regarded as a characteristic property of the crystalline state, at least under ideal conditions Not only is this true in respect of such vibrations as are also observable with the substance in the molten or dissolved condition, but it is equally so in respect of such vibrations as are specially characteristic of the crystalline state It is obviously impossible to reconcile this situation with the idea that these vibrations are of the same nature as the elastic vibrations giving a continuous spectrum of frequencies

To exhibit the fundamental error in Born's postulate, we may consider the behaviour of a model consisting of N Planck oscillators of identically the same kind regularly arranged in geometric order inside a box The postulate of Born assumes that the dynamic behaviour of these oscillators could be represented by a three-dimensional Fourier series whose wavelengths are sub-multiples of the dimensions of the box and in which all the terms have equal weight The assumption is, *prima facie*, unjustifiable because we are not here concerned with possible translatory movements of the oscillators which would involve collisions with the walls of the box, but only with the internal oscillations of the individual units in fixed positions. Accepting the postulate however for a moment, we may consider its implications in regard to the behaviour of the oscillators in our model The essence of a Fourier representation is that the summation of the terms can reproduce the most arbitrary kind of disturbance In the present case, since the series contains the full number of terms, namely N , all of which have equal weight, it would mean that their superposition would result in the phases of the individual oscillators being entirely arbitrary and uncorrelated with each other This is evidently a *reductio ad absurdum*, since such a state of affairs could only exist when the Planck oscillators are entirely independent of each other, as would be the case if we were considering the molecules of a gas It is a fundamental aspect of the crystalline state that the oscillators of which it is composed are coupled to each other more or less firmly In diamond, for example, the bonds connecting the different lattice cells with each other are exactly of the same kind as those

which bind the atoms within the cell. The proposition that the internal oscillations occurring in the neighbouring cells of the lattice are uncorrelated in phase is thus entirely indefensible. Indeed, it would be more reasonable to make exactly the contrary assumption, namely that the phases of the oscillations in neighbouring cells are so highly correlated with each other that to all intents and purposes, the entire piece of diamond functions as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency. Only on some such view could we hope to understand the extraordinarily perfect monochromatism of the lattice vibrations in diamond.

We may summarise the situation by stating that the Born postulate does not represent the true state of affairs in a crystal except in regard to the low-frequency elastic vibrations, in which case, of course, it is of no particular significance. The real state of affairs in a crystal demands that if the distribution of phase of the Planck oscillators in a specified volume could be represented as a three-dimensional Fourier series, only the terms which have wave-lengths large compared with the lattice spacings and orientations specifically related to the geometry of the crystal structure would be allowed, while terms with phase wave-lengths of the same order as the lattice spacings would be altogether excluded. The stronger the atomic forces and the tighter the resultant mechanical coupling between the lattice cells, the more nearly would we approach a state of affairs in which the entire crystal behaves as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency.

6 Fundamental Defects of the Existing Theories

Born's postulate of the cyclic lattice which has been discussed in the foregoing pages and shown to be untenable was the basis on which Debye, Waller and Laue developed their treatments of the problem of the temperature effect in X-ray diffraction. It follows that, quite apart from the incompetence of the classical mechanics to deal correctly with the problem, these earlier investigations were also otherwise fundamentally defective, being in fact based on an erroneous conception of the nature of the vibrations in a crystal lattice. The picture of the X-ray phenomena which they present differs radically from the truth, failing as it does to indicate the fundamental difference between the low-frequency or continuous spectrum of elastic vibrations and the high-frequency or monochromatic vibrations in the infra-red, in respect of the X-ray effects to which they give rise. This is not surprising as the theories start from the assumption that these modes of vibration are essentially similar.

To make the foregoing points clear, we proceed to show from first principles how essentially the X-ray effects due to these two types of vibration of the lattice must differ. We shall consider first the elastic vibrations of the crystal lattice. These involve translatory movements of the lattice cells of the crystal from their positions of equilibrium. It is evident that if there are N lattice cells in the crystal, such translations would involve $3N$ degrees of freedom. They may therefore be regarded as due to the superposition of $3N$ sets of elastic waves of all the possible wave-lengths and frequencies, these having equal weight. It follows that the movements of any individual cell resulting from such superposition would be uncorrelated with that of any other lattice cell in the crystal. Hence, the secondary radiations of modified frequency sent out from the individual cells would be incoherent. In other words, the elastic vibrations would result in a secondary radiation of which the aggregate intensity is proportional to the number of lattice cells and which is in the nature of a diffuse or scattered radiation. This argument is not invalidated by the fact that the oscillation of a *particular* frequency expressed by one of the terms in the Fourier representation has a specifiable phase-relation in respect of the different lattice cells. The contradiction disappears when we remember that the number of degrees of freedom allotted to a *particular* frequency in a continuous spectrum is only one out of the very large number N . Hence, in spite of the fact that an elastic vibration of a specified frequency may be considered to be a coherent type of oscillation, the effect of all such vibrations taken together is essentially an incoherent radiation or diffuse scattering of which the intensity is proportional to N the number of lattice cells and not to N^2 .

The position is entirely different when we consider the monochromatic vibrations of the lattice cells. The monochromatism implies that all the N degrees of freedom refer to a single mode of oscillation, which in the limiting case is pictured as having identically the same frequency, amplitude and phase in all the lattice cells of the crystal. The movements of the atoms within a cell results in secondary radiations from the atoms, and therefore also from the cells, possessing components of modified frequency. The identity of the oscillation in all the lattice cells ensures that these secondary radiations received at any external point have coherent phase-relationships. Hence, these are capable, exactly as in the case of the secondary radiations of unmodified frequency, of giving rise to interference effects. Indeed, it is clear that they would result in a *geometric reflection of the X-rays by the lattice planes of the crystal but with modified frequency*. In the limiting case when all the cells vibrate in identical phase, the direction in

which this modified geometric reflection would appear is the same as that of unmodified reflection

We thus see that the elastic vibrations of the solid and the infra-red vibrations of the lattice cells give rise to X-ray effects which are fundamentally different and which, in fact, portray in a geometric form the radically different spectroscopic characters of the two modes of vibration. The elastic vibrations give a diffuse scattering of the incident X-rays with an intensity proportional to N , the number of lattice cells, while the infra-red vibrations give geometric reflections of altered frequency of which the intensity (subject to the same limitations as in the case of the unmodified reflections) is proportional to N^2 . It will be noticed that these results are consequential on our rejection of the Born postulate. Had the latter been valid, both types of vibration would have given a diffuse scattering proportional to N , the number of lattice cells, this, in fact, is the result emerging from the investigations of Debye, Waller and Laue, except that the actual result due to the elastic vibrations appears exaggerated in their papers by the assignment to them of $3pN$ degrees of freedom instead of $3N$ the correct number, p being the number of atoms in the unit cell of the lattice. That the internal vibrations within the lattice cells are not considered at all is clear from Laue's memoir where the positions of the atoms within the unit cell are explicitly regarded as constants.

7 *Quantum Reflection of X-Rays*

The preceding discussion enables us to proceed further and give a quantitative picture of the geometric reflection of X-rays by the lattice planes of a crystal with altered frequency. We consider the individual cells of the crystal lattice as Planck oscillators of frequency ν^* , so that, when excited, the energy of each oscillator is $h\nu^*$. An oscillation with this energy would result in the atoms in the cell being set in vibration such that the sum total of their kinetic energies in passing through the position of equilibrium is equal to $h\nu^*$. We then write down the expressions for the secondary radiations of various frequencies from each of the atoms in the cell. These are then summed up in the usual way, taking the positions of the atoms into account, to find the structure factor of the lattice cell. *This is done separately for each of the different frequencies of secondary radiation.* If the frequency ν^* is sufficiently high in relation to the temperature of the crystal, in other words, if $h\nu^* \gg kT$, it is sufficient to consider only the component having the primary or unmodified frequency ν and the component with diminished frequency $(\nu - \nu^*)$. Assuming that the setting of the crystal is such that the Laue conditions are satisfied for a particular set of lattice

planes, it would follow that the primary X-rays of frequency ν would then be reflected by these planes. Simultaneously, the modified radiations of frequency $(\nu - \nu^*)$ would also be reflected by the same planes and in the same direction, provided we assume that the phase of the vibration of frequency ν^* is the same for all the cells in the crystal. The intensity of the modified reflection of frequency $(\nu - \nu^*)$ would be determined by the dynamic structure factor of the lattice cell, in exactly the same way that the intensity of the unmodified reflection of frequency ν is determined by the static structure factor.

It will be noticed that this argument assumes that each of the N cells of the lattice is excited with an energy $h\nu^*$. It might seem at first sight that this would involve the entire crystal abstracting an energy $Nh\nu^*$ from the energy $h\nu$ of the incident X-ray photon, which of course, is impossible, besides being inconsistent with the assumed frequency $(\nu - \nu^*)$ of the reflection. Actually, all that the argument assumes is that the crystal functions as a single oscillator of frequency ν^* but with a statistical weight N times greater than that of a single lattice cell. This of course is only possible when all the cells vibrate in identically the same way, as is actually assumed in the argument. The intensity of the reflection calculated in this way would be the maximum possible. It may be regarded as an estimate of intensity to be expected in the most favourable setting of the crystal, viz., when the Laue conditions are satisfied also for the unmodified reflection. It may be emphasized that the quantum reflection is the result of a transition of the crystal from the ground state to a higher energy level of vibration, the energy required for the transition being derived from the incident radiations themselves and not from the energy of the thermal agitation of the crystal. Indeed in the circumstances considered, namely when $h\nu^* \gg kT$, thermal agitation is non-existent and can therefore play no part in the phenomenon. It may be remarked also that the so-called zero point energy which finds a place in the earlier semi-classical investigations of the X-ray problem becomes irrelevant from our present point of view.

8 *Quantum Scattering of X-Rays*

We now proceed to consider the X-ray effects arising from the elastic or low-frequency vibrations of the crystal lattice. As already remarked, these vibrations displace the lattice cells as a whole from their positions of equilibrium. Considering an elastic vibration of a particular wave-length, we notice that the stratifications in the medium arising from it are of two distinct kinds. Firstly, the elastic wave may itself, if it be of the longitudinal type, be regarded as a periodic stratification of electron density in a medium

which may otherwise be considered as uniform. This view of the matter is appropriate when we are concerned with stratifications with a spacing greater than the largest grating intervals in the crystal. Secondly, the elastic waves, more particularly those of the transverse type, disturb the regular arrangement of the lattice cells, so that the structure amplitudes of the crystal plane are diminished and, *per contra*, new dynamic stratifications are created due to the superposition of the elastic waves and the static crystal planes. This is the point of view developed in detail in Laue's memoir. The scattering of the X-rays by either of the processes indicated would necessarily involve a change of frequency. The scattering by the elastic waves themselves would appear in directions making smaller angles with the primary X-ray beam (assumed to be monochromatic) than the scattering due to their combinations with the crystal spacings. The two effects together give the background or diffuse scattering of X-rays by the crystal.

Since the elastic vibrations are of relatively low frequency, the situation may be represented in the majority of such cases by the inequality $h\nu^* \ll kT$, ν^* being the frequency of elastic vibration. When this is the case, the results to be expected from the classical and quantum theories would be identical. In other words, the effects observed may be described as the result of each of the elastic modes of vibration possessing an energy kT , the scattered radiations appearing with equal intensity in the two frequencies $(\nu \pm \nu^*)$. It must not be assumed, however, that a treatment on these lines would represent the facts of X-ray scattering in every case. Whenever the elastic frequency ν^* under consideration is high or the temperature T of the crystal is low so that $h\nu^* \gg kT$, the situation would be reversed. The intensity of X-ray scattering would then be the result of assigning an energy $h\nu^*$ to each vibration, and it follows that it would then be much greater than that given by the classical considerations. Since the energy is abstracted from the incident quantum, the scattered radiation would then appear only with diminished frequency $(\nu - \nu^*)$. It is evident also that the semi-classical considerations based on the Planck specific heat formula and the existence of zero point energy of the kind which figure in the earlier X-ray investigations cannot describe the situation correctly and are therefore irrelevant.

9 Characters of the Two Effects

It is evident from the foregoing discussion that the effects arising respectively from the vibrations in the infra-red and the elastic ranges of frequency are entirely different. Numerous criteria present themselves which make it possible to distinguish the one from the other.

Firstly—The geometric distribution of the secondary X-radiations is widely different in the two cases, being a regular reflection of the incident X-rays by the lattice planes in one case and a diffuse scattering in the other. The influence of the setting of the crystal on the two phenomena is determined by considerations of a wholly distinct kind and should therefore also be quite different.

Secondly—The intensity in one case is proportional to N^2 , viz., the square of the number of effective lattice cells and in the other case to N . Variations of the thickness of the crystal plate and of the cross-section of the X-ray beam traversing it would therefore influence the two phenomena in entirely different ways.

Thirdly—The dynamic structure amplitudes for the quantum reflections are determined by the modes of atomic vibration and are not necessarily proportional to the static structure amplitudes. It is quite possible, for instance, that the dynamic structure amplitude for a particular set of crystal planes is zero while the static structure amplitude for the same planes is finite, or *vice versa*. In other words, the intensities of the classical and quantum reflections by any given set of crystal planes are not necessarily proportional to each other. Such a situation cannot arise in the quantum scattering of the X-rays, as this is due to the simple translatory movements of the lattice cells.

Fourthly—Since the two phenomena arise from vibrations of the crystal lattice lying in widely different ranges of frequency, their intensity variations with temperature would be markedly different. In either case, a finite limiting intensity would be reached at low temperatures, but this would be far greater relatively to the intensity at ordinary temperatures for the infra-red vibrations than for the elastic ones.

Fifthly—The characters of the quantum reflections and their variation with physical conditions such as temperature should exhibit a close correlation with the spectroscopic behaviour of the substance in the infra-red region, the quantum scattering, on the other hand, should show a correlation with the elastic behaviour of the substance.

Sixthly—The changes of frequency, if directly observable, would naturally be much greater for the quantum reflections than for the quantum scattering.

10 Summary

The paper examines the views generally current at the present time regarding the nature of the vibrations possible in a crystal lattice which

are based largely on the specific heat theory of Debye and the crystal dynamics of Max Born and his school. The latter has for its starting point the so-called postulate of the "cyclic lattice". It is here shown that this postulate is an *ad hoc* supposition adopted for mathematical convenience and that, far from being justifiable, its consequences are definitely contradicted by the known spectroscopic behaviour of crystals and that it is also contrary to the dynamic behaviour which should be expected from a set of coupled Planck oscillators such as the lattice cells of a crystal constitute. It is also shown that the modes of vibration of the elastic type forming a continuous spectrum and the modes of vibration having discrete or monochromatic frequencies in the infra-red region have fundamentally different dynamic characters. Starting from the proposition established by Laue that the secondary X-radiation from an oscillating atom exhibits components of modified frequency, it is shown how the resultant effects of the secondary radiations of modified frequency due respectively to these two types of vibration can be evaluated. It is shown further that the infra-red vibrations result in geometric reflections by the lattice planes of the crystal but with altered frequency, their intensity (subject to the same limitations as for the classical reflections) being proportional to N^2 , that is, to the square of the number of lattice cells in the crystal. On the other hand, the elastic vibrations of low frequency give a diffuse scattering of the X-rays of which the intensity is proportional to N . As both these effects involve changes of frequency, the classical mechanics is incompetent to describe them correctly, and has therefore to be replaced by quantum-mechanical considerations. It is shown how this can be done quantitatively. The temperature dependence of both these effects is discussed. Finally, numerous experimental criteria are presented distinguishing the two effects which should prevent them from being mistaken for each other.

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QUANTUM THEORY OF X-RAY REFLECTION: MATHEMATICAL FORMULATION

BY SIR C V RAMAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

As was pointed out by Laue (1926), the secondary radiations from the atoms in a crystal traversed by a monochromatic beam of X-rays suffer changes of frequency when the atoms oscillate about their positions of equilibrium. These changes of frequency play a fundamental rôle in determining the observed X-ray phenomena. For, the superposition of radiations which differ in frequency cannot give rise to observable interferences, while, on the other hand, secondary radiations of identical frequency are necessarily coherent and capable of interfering with each other even if the frequency differs from the primary X-ray frequency. Accordingly, if we fix our attention on a particular mode of vibration of the atoms in a crystal, the radiations of altered frequency arising therefrom can give rise to interference maxima in just the same way as the radiations from stationary atoms. It follows also, that if several vibrations co-exist in a crystal, each set of secondary radiations of different frequency thus arising would produce its own interference maxima independently of the others. If, further, the individual vibrations are of infinitesimal amplitude, a considerable simplification becomes possible. For, then each vibration may be regarded as giving rise to its own secondary radiations and acting independently of all the others, provided its frequency is different from theirs. This statement, however, requires some qualification when the excursions of the atoms about their positions of equilibrium

resulting from the totality of all the vibrations present have a finite amplitude. For, the total radiation amplitude of an atom is fixed and is equal to the superposed radiation amplitudes of various frequencies. Hence, the radiation amplitude due to any particular vibration frequency would naturally be less than it would be in the absence of all the others. It is evident also that as the atomic excursions increase, the strength of the secondary radiations of the original or primary X-ray frequency and of the interference maxima to which they give rise must progressively diminish, finally tending to zero.

The elastic or low-frequency modes of vibration have a continuous spectrum of frequencies and hence, as explained above, the optical effects of each vibration should be considered separately. Since the energy corresponding to a particular frequency is small and is further distributed over all the atoms in the crystal, the resulting atomic amplitudes are exceedingly small. Hence, the secondary radiations due to these separate vibrations are exceedingly weak, and since they are incoherent, their intensities and not their amplitudes should be added. In the final result, therefore, we have an effect which is inherently feeble and which can only become important when a large volume of the crystal is under consideration.

The position is different when we consider the effect of modes of vibration of the crystal which appear as monochromatic frequencies in its infra-red spectrum. Each such line in the spectrum represents N co-existent modes of vibration, where N is the number of the lattice cells in the crystal. In the ideal case when all the N modes are of identical frequency, it is evident that the secondary radiations of altered frequency due to these co-existing modes would all be coherent and must therefore be considered *together* and *not separately*. It is evident, therefore, that the vibrations of the infra-red type can give rise to effects of an altogether higher order of intensity than the elastic vibrations considered above. This result has already been deduced in an earlier paper from a consideration of the phase relations subsisting between the lattice cells in a crystal in an infra-red vibration. Its possibility, it may be remarked, is consequential on our rejection of the ideas of Debye and Born regarding the nature of the high frequency vibrations in a crystal lattice, and especially of the so-called postulate of the "cyclic lattice" due to Born which we have considered in detail and shown to be untenable.

It should be noted that the elastic and infra-red modes of vibration of a crystal also differ in other respects. In the former case, the basic grouping of the atoms in the lattice cells remains unaltered, while in the latter, it is to be regarded as essentially a variable. Then again, the wave-fronts of an elastic vibration may have any possible orientation within the crystal, while for the infra-red vibrations, there is *prima facie* no reason for assuming that this

should be the case. It has also to be remembered that the elastic vibrations are of lower frequency than the infra-red ones, this makes a considerable difference in considering the influence of thermal agitation in the two cases.

As already explained in the preceding paper, the recognition of the changes of frequency, the importance of which was first emphasised by Laue, leads us naturally to bring the X-ray problem within the scope of the quantum theory of radiation. It also makes the transition from the classical to the quantum mechanical considerations very simple. The changes of frequency indicated by the classical electrodynamics appear in the quantum theory as the result of exchanges of energy between the quantum and the crystal lattice. Similarly, the Laue conditions for a dynamic reflection are the same as those required for the conservation of momentum in the encounter between the quantum and the crystal. The principal difference between the classical and quantum points of view is in regard to the question of the absolute intensity of the secondary radiations and its dependence on temperature. Here, the quantum mechanical considerations replace such incorrect applications of the quantum theory to X-ray physics as are usually made by introducing the Planck factor and the zero point energy, neither of which is really relevant when considering the exchanges of energy between matter and radiation.

2 Secondary Radiations from an Oscillating Atom

Under the influence of waves of unit amplitude, an atom emits secondary radiations which at a distance R from the origin of co-ordinates and in a direction making an angle 2ψ with the primary ray have the amplitude

$$f \sin \beta \frac{e^2}{mc^2} \frac{1}{R} \cos 2\pi \left(\nu t - \frac{R + 2D \sin \psi}{\lambda} \right), \quad (1)$$

where D is the perpendicular distance of the atom from a reference plane through the origin bisecting the angle between the primary and secondary rays, f is the atomic structure factor, and β the angle between the electric vector in the incident pencil and the diffracted ray. It is evident that this expression would remain invariable if the atom moves parallel to the reference plane but would alter periodically if it oscillates perpendicular to it.

Writing

$$D = d + a \cos (2\pi \nu^* t + z) \quad (2)$$

the periodic part of (1) may be written as

$$\cos [2\pi \nu t - Z - \zeta \cos (2\pi \nu^* t + z)] \quad (3)$$

where

$$Z = \frac{2\pi (R + 2d \sin \psi)}{\lambda}, \quad \zeta = \frac{4\pi a \sin \psi}{\lambda}. \quad (4)$$

The expression (3) may be expanded in a series of Bessel functions. Neglecting

the functions of higher order than the first, it may be written as

$$J_0(\zeta) \cos(2\pi\nu t - Z) + J_1(\zeta) \sin[2\pi(\nu \pm \nu^*)t - Z \pm z] \quad (5)$$

The three quantities Z , ζ and z appearing in (5) are all phase angles. Z is the phase of the secondary radiation from the atom when it is in the position of equilibrium, ζ the change of this phase produced by displacing the atom through a distance a in a direction normal to the reference plane, and z is the phase of the atomic vibration. Expression (5) indicates that the secondary radiation from the oscillating atom consists of three components whose amplitudes depend on the amplitude of the oscillation and which differ in frequency and phase. The first component has the frequency ν of the primary X-rays and its phase is determined solely by the equilibrium position of the atom. Its amplitude has however been diminished by the movement of the atom in the ratio $J_0(\zeta)/1$. The second and third components have the same amplitude, namely $J_1(\zeta)$, but they differ in frequency and phase. The component $(\nu + \nu^*)$ has a phase angle $(Z - z)$, while the component $(\nu - \nu^*)$ has a phase angle $(Z + z)$. The secondary radiations of altered frequency thus increase in amplitude with increasing vigour of the atomic vibration, while their phases are determined jointly by the atomic positions and the phase of the atomic vibrations. The equality of the amplitudes of the components of increased and diminished frequency indicated by (5) is a typical consequence of the classical electrodynamics which will later be amended in the light of quantum mechanics.

3 Dynamic Stratifications of Density

We may now proceed to deduce the optical effect of all the atoms vibrating with the same frequency but with a phase which may be assumed to vary slowly from place to place within the crystal. For the purpose of a graphical derivation of the conditions for interference, it is not necessary at the present stage to distinguish between the elastic and infra-red modes of vibration. We consider a particular set of lattice planes in the crystal marked $d d d$ in the figure

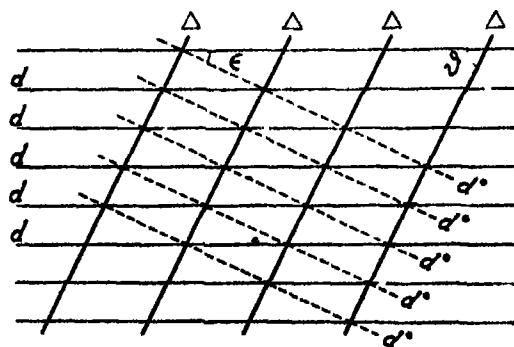


FIG. 1
Graphical Derivation of the Dynamic Spacings

It is evident that for any given setting of the crystal the phase of the secondary radiations as received at a distance will vary from point to point within the crystal. In respect of the secondary radiations of unmodified frequency, this phase is given by Z . Hence, to obtain the maximum resultant intensity, Z must be invariable along a crystal plane and jump by 2π or an integral multiple thereof, as we pass from plane to plane. In other words, the planes ddd should make equal angles with the incident and diffracted rays, and their spacing d should satisfy the relation

$$2d \sin \theta_c = \lambda \quad (6)$$

This is the familiar optical formula for a monochromatic reflection from a regularly stratified medium. θ_c indicates the glancing angle for a classical or unmodified reflection.

Considering now the secondary radiations of altered frequency, we see that their resultant is determined by the variation of $(Z - z)$ in one case and of $(Z + z)$ in the other. Let $\Delta\Delta\Delta$ in the figure represent the planes along which the phases of the atomic vibrations, in other words the values of z , are constant. In order to obtain the maximum intensity for the resultant of the secondary radiations, the crystal should be so set that $(Z - z)$ or $(Z + z)$ as the case may be, is constant along the lattice planes, it is evident from the figure that this would be the case if the setting of the crystal is such that the incident and diffracted rays are equally inclined to the planes which run diagonally cutting the ddd and $\Delta\Delta\Delta$ planes, e.g., $d^*d^*d^*$ as shown in Fig 1. For obtaining the maximum intensity, a further condition must be satisfied, namely

$$2d^* \sin \psi = \lambda, \quad (7)$$

where ψ is, as before, half the angle between the incident and diffracted rays. It is evident from the figure that there are two sets of diagonal planes possible. But the same set will satisfy equation (7) for both the frequency components $(\nu + \nu^*)$ and $(\nu - \nu^*)$, provided that we assume the phase angle Z advances in one case and recedes in the other case as we move across the figure. The diagonal planes $d^*d^*d^*$ thus represent the dynamic stratifications of electronic density resulting from the vibrations of the atoms contained in the lattice planes of the crystal. As the phase waves $\Delta\Delta\Delta$ move from left to right, the dynamic stratifications $d^*d^*d^*$ move upwards, keeping a constant spacing, while if the phase waves $\Delta\Delta\Delta$ move from right to left, the spacings $d^*d^*d^*$ move downwards in the same way. The changes of frequency from ν to $(\nu \pm \nu^*)$ may thus be regarded as analogous to the Doppler effect in the reflection from a moving mirror.

4. Geometric Law of Dynamic Reflection

The spacing d^* of the dynamic stratifications is connected with the spacing d of the static ones and the phase-wave length Δ of the atomic vibrations by the vectorial relation,

$$\frac{\vec{1}}{d^*} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta}. \quad (8)$$

This is readily deduced by writing down the vectorial equation represented by the three sides of one of the triangles appearing in Fig 1 and dividing the same by the area of the triangle Denoting by ϑ the angle between the planes $d d d$ and the phase waves $\Delta \Delta \Delta$, and by ϵ the angle between the planes $d d d$ and $d^* d^* d^*$, we have from Fig 1 and equation (8)

$$d^* \sin \vartheta = d \sin (\vartheta \pm \epsilon) = \Delta \sin \epsilon \quad (9)$$

Substituting the first of these relations in (7), we obtain

$$2 d \sin \psi \sin (\vartheta \pm \epsilon) = \lambda \sin \vartheta \quad (10)$$

Equation (10) is the general geometric law of dynamic reflection deduced by Raman and Nath (1940) It will be noticed from (9) that when the phase wave-length Δ is infinite, $\epsilon = 0$ and $d^* = d$, from which it follows that $\psi = \theta$. In other words, the static and dynamic reflections then coincide in direction This is also obvious directly from Fig 1 In general, however, d^* and d are different, and the conditions for the possibility of static and dynamic reflections are not the same. While a static reflection can only occur at the particular setting of the crystal indicated by (6), a dynamic reflection is evidently possible over a wide range of settings of the crystal determined by the permissible values of the phase wave-length Δ It is further to be remarked that while the glancing angles of incidence and reflection are equal for the static reflections given by (6), these angles when measured as usual with reference to the static crystal planes would generally differ from each other for the dynamic reflections Further, the latter reflections would in general appear in a plane different from that of the incidence of the X-rays on the crystal spacings. To specify the actual plane of dynamic reflection, it is necessary to know the angle χ which determines the azimuth of the phase waves. We may put $\chi = 0$ in the case when the dynamic reflection appears in the plane of incidence, the phase waves then being evidently perpendicular to that plane. When $\chi \neq 0$, the dynamic reflection swings out of the plane of incidence to an extent determined by the values of Δ , ϑ and χ

In the particular case when $\chi = 0$, it is evident that

$$\phi + \theta = 2 \psi, \text{ and that } \phi - \theta = 2 \epsilon, \quad (11)$$

where θ and ϕ are respectively the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Equation (10) may then be written as

$$2d \sin \frac{\theta + \phi}{2} \sin \left(\vartheta \pm \frac{\theta - \phi}{2} \right) = \lambda \sin \vartheta \quad (12)$$

The value of ϕ then depends on the angle ϑ . If we imagine ϑ to march from 0 to π , equation (12) shows that the relation between ϕ and θ will alter from

$$\phi = \theta, \text{ when } \vartheta = 0 \text{ or } \pi \quad (13)$$

to

$$d(\sin \theta + \sin \phi) = \lambda, \text{ when } \vartheta = \frac{\pi}{2}. \quad (14)$$

Thus, when the phase waves are *parallel* to the crystal planes, the dynamic reflection always satisfies the ordinary geometric law of reflection from the crystal planes, while if the phase waves are transverse to the crystal planes, it appears in the direction given by (14) which may be written *approximately* as

$$2d \sin \frac{\theta + \phi}{2} = \lambda \quad (15)$$

thereby indicating that the angle between the incident and reflected rays is approximately constant and independent of the crystal setting

5 Dynamic Structure Factor

To find the conjoint effect of the secondary radiations from all the atoms in the unit cell of the lattice, we have to sum them up considering each component of frequency separately. This summation for the radiations having the primary X-ray frequency gives (omitting constant factors),

$$\sum_p J_p J_0(\zeta_p) \cos(2\pi \nu t - Z_p) \quad (16)$$

The summation for the secondary radiations of frequency $(\nu \pm \nu^*)$ similarly gives

$$\sum_p J_p' J_1(\zeta_p') \sin[2\pi(\nu \pm \nu^*)t - Z_p' \pm z_p'] \quad (17)$$

the index p referring to the p th atom in the cell, and the dashes in (17) indicating that the setting of the crystal and the angle of diffraction are not necessarily the same as those considered in (16). Remembering, however, the conditions for a dynamic reflection discussed in the foregoing section, namely that $Z \pm z$ should be constant along any particular lattice plane, we may simplify (17) and write it in the form

$$\sum_p J_p' J_1(\zeta_p') \sin[2\pi(\nu \pm \nu^*)t - Z_p] \quad (18)$$

Z_p having now the same significance as in (16) for a static reflection by the same set of lattice planes. A further simplification arises when the angle between the primary and diffracted radiations does not differ greatly for (16) and (18). We may then write, approximately, $J_p' = J_p$. If, further, the setting of the crystal in the two cases is not so greatly different, we may also write, $\zeta_p' = \zeta_p$, as an approximation. Subject to the restrictions indicated, (17) now takes the form

$$\sum_p J_p J_1(\zeta_p) \sin [2\pi(\nu \pm \nu^*)t - Z_p] \quad (19)$$

The static structure factor of the unit cell as influenced by the particular vibration may therefore be evaluated by diminishing the structure factor of each atom in the ratio $J_0(\zeta_p)$ to unity. At the same time, the lattice cell acquires a dynamic structure factor which is found in exactly the same way except that the structure factor of each atom is now multiplied by $J_1(\zeta_p)$.

Very significant differences now arise in considering respectively the elastic and the infra-red vibrations. For the elastic vibrations, ζ_p is the same for all the atoms in the unit cell. The suffix p may therefore be removed and the Bessel functions taken outside the summation sign. For an elastic vibration, therefore, the static and dynamic reflections may be evaluated from the expressions

$$J_0(\zeta) \sum_p J_p \cos(2\pi\nu t - Z_p) \quad (20)$$

$$J_1(\zeta) \sum_p J_p \sin[2\pi(\nu \pm \nu^*)t - Z_p] \quad (21)$$

The static and dynamic structure factors in the case of an elastic vibration thus differ only by a multiplying factor which is the same for all the atoms in the unit cell. Thus, if a particular set of crystal planes gives zero intensity for a particular order of reflection, the dynamic reflections for the same planes and the same order of reflection must also vanish. The dynamic reflections by different sets of crystal planes would follow the same order of intensity as the static reflections by those planes, provided the amplitude of the elastic vibrations transverse to the planes may be assumed to be the same. A similar remark would also apply to the relative intensities of the successive orders of reflection by a particular set of planes, except that the factor $J_0(\zeta)$ diminishes while the factor $J_1(\zeta)$ increases as the angle of diffraction becomes larger, *vide* equation (4).

The position is greatly altered when we consider the infra-red vibrations of the lattice. Here, the displacements being different for the different atoms, the factors $J_0(\zeta_p)$ and $J_1(\zeta_p)$ must remain within the summation signs. Some of the atoms in the lattice cell must evidently move in directions opposite to

the others if the centre of gravity of the cell is to remain undisplaced. Hence $J_1(\zeta_p)$ would be positive for some of the atoms and negative for the others in an infra-red vibration, while on the other hand $J_0(\zeta_p)$ would always be positive and nearly equal to unity. It follows that the static and dynamic structure factors for an infra-red vibration are determined by quite different considerations and cannot, in general, exhibit the close parallelism indicated by the theory for the elastic vibrations. Indeed, it may well happen that in particular cases, the static structure factor vanishes while the dynamic structure factor remains finite, or *vice versa*.

6 Quantum Scattering by Elastic Vibrations

The disturbance produced by an elastic vibration on X-ray propagation is of two kinds. Firstly, a compressional wave would evidently alter the average electronic density. It is thus itself a dynamic stratification of the medium capable of reflecting the X-rays with a frequency $(\nu \pm \nu^*)$, increased or decreased as the case may be, depending on the direction of the wave. Such a reflection occurs when

$$2\Delta \sin \psi = \lambda, \quad (22)$$

large values of Δ corresponding to small values of ψ , and *vice versa*. Thus, since Δ may have any one of a practically continuous series of values determined by the dimensions of the crystal, and since the orientation of the wave is arbitrary, the reflection indicated by equation (22) would result in a cone of scattered X-rays (the Brillouin cone) having the direction of the primary beam as its axis. The angular extension of the cone depends on the smallest permissible values of Δ . The intensity of such scattering would depend on the energy of the vibration and the resulting variation of electron density. On the classical mechanics, the energy of an elastic vibration of thermal origin may be taken as KT , while if the wave is quantum-mechanically excited by the incident radiation, the energy would be $h\nu^*$. The latter assumption would be the appropriate one to make if $h\nu^* \gg KT$, while if $h\nu^* \ll KT$, the former assumption would be correct. This type of X-ray scattering should therefore be exhibited by crystals even at the lowest temperatures and in the absence of thermal agitation, and especially by crystals of high elasticity, e.g., diamond. We should expect the intensity of the X-ray scattering by such crystals to be greater than that indicated by the classical considerations even at ordinary temperatures.

The second kind of disturbance to X-ray propagation arises from the distortions which the elastic waves cause to the regular stratifications of the crystal structure. The formulæ of the three preceding sections enable us to evaluate these effects quantitatively in a very simple manner. As explained

in Section 3 and illustrated in Fig 1, the superposition of an elastic vibration on a specified set of crystal planes gives rise to dynamic stratifications of density. As further explained in Section 4, these stratifications reflect the incident X-rays in the direction given by the general geometric law (10). The intensity of such reflection is determined by the dynamic structure factor as explained in Section 5.

Considering the *direction* in which the so-called dynamic reflection appears, it is evident from equations (9) and (10) that this depends on the wave-length Δ , the angle ϑ which the wave-fronts make with the crystal spacings, and also upon the azimuth χ of the wave-fronts. A variation of χ would throw the dynamic reflection out of the plane of incidence, while if $\chi = 0$, the reflection would appear in that plane. A dynamic reflection is only possible when the X-ray wave-length, the dynamic spacing d^* and the glancing angle ψ of incidence of the X-rays thereon are suitably related. But since we have at our disposal two variables, namely Δ and ϑ , we may, as is evident from Fig 1, by suitably altering both of them get a dynamic reflection *in any desired direction*. In other words, the resultant effect of all the elastic vibrations is a diffuse scattering of the X-rays over a wide range of solid angles and not a geometric reflection in any specified direction.

To find the X-ray scattering due to any particular set of crystal planes, we have only to evaluate the two expressions (20) and (21) given previously. Their magnitudes are in the ratio $J_0(\xi)/J_1(\zeta)$. If ζ be sufficiently small, $J_0(\zeta)$ is practically unity while $J_1(\zeta)$ would be equal to $\frac{1}{2}\zeta$. If m be the mass of an unit cell of the lattice, the energy of vibration of N such cells, each having an amplitude a with a frequency ν^* would be $2\pi^2 mNa^2\nu^{*2}$. This may be written in the form $2\pi^2 M\sigma^2 \cdot a^2/\Delta^2$, where M is the mass of the whole crystal, σ is the velocity of the elastic waves and Δ is their wave-length. Utilising equations (4), (7) and (9), we may write this in the simple form

$$\frac{1}{2}\zeta^2 = M\sigma^2 \sin^2 \epsilon / \sin^2 \vartheta \quad (23)$$

This may now be put equal to KT (classical mechanics). Accordingly, we have

$$\frac{1}{2}\zeta^2 = KT/M\sigma^2 \sin^2 \vartheta / \sin^2 \epsilon \quad (24)$$

Equation (24) gives the ratio of the sum of the squares of the dynamic structure factors to the square of the static structure factor. It is evidently of the order $1/N$ and is thus an exceedingly small quantity. The X-ray scattering in any specified direction due to the distortion of the crystal planes by the elastic waves is therefore of vanishingly small intensity in comparison with the intensity of regular reflection by the same crystal planes and should be unobservable except when relatively large volumes of the crystal are under consideration.

The numerical factor $\sin^2\theta/\sin^2\epsilon$ appearing in equation (24) determines the manner in which the intensity of the scattered radiation varies with direction. It may be written also as Δ^2/d^{*2} , where Δ and d^* have the same significance as in equation (8). Thus the intensity of the scattering would be greatest in those directions for which the wave-length Δ of the elastic waves which effectively scatter the X-rays is greatest. This variation arises because the amplitude of the elastic waves is directly proportional to their wave-length, and the scattering is therefore greatest in the directions in which the waves of longest wave-length and lowest frequency are effective. The nature of the variation can be readily made out from Fig. 2, which represents the geometric relation between $1/d$, $1/d^*$ and $1/\Delta$ given by equation (8), as also the relation between $1/d^*$, $1/\lambda$ and $\sin\psi$ expressed by equation (7).

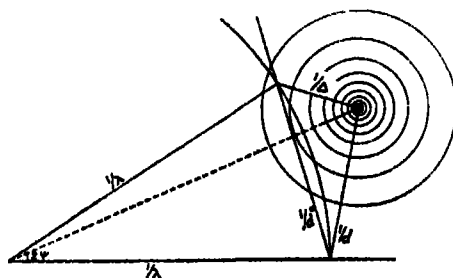


FIG. 2

Distribution of Intensity of Diffuse X-Ray Scattering

Spheres are drawn (sections of which by the plane of the figure appear as circles) round the terminus of the vector $1/d$ and with radii $1/\Delta$, points on the spheres represent various values and orientations of the vector $1/\Delta$ drawn from their common centre. The spheres are drawn closely together near their centre and further away at a distance from it to suggest the rapid diminution of the amplitude of the elastic waves with diminishing wave-length. A sphere of reflection is drawn with radius $1/\lambda$ around O as centre. It cuts across the "spheres of diffusion" having the radii $1/\Delta$ and the scattered radiations would therefore appear over the entire area of the sphere of reflection thus cut by the spheres of diffusion. When the sphere of reflection actually passes through the terminus of the vector $1/d$, the maximum of scattering intensity would fall on the sphere itself, but as it would then coincide with the regular reflection, the maximum would be unobservable. In other cases, the scattering would show a very broad and diffuse maximum of intensity corresponding to the minimum value of $1/\Delta$ on the sphere of reflection. This maximum however becomes rapidly weaker and more diffuse as the sphere of reflection passes further away from the centre of the spheres of diffusion with altered settings of

the vector $1/d$. Hence, nothing even remotely resembling a regular geometric reflection which persists over a wide range of settings of the crystal would be exhibited by the X-ray scattering due to the elastic waves

The same situation can be represented graphically by plotting the function $\sin^2 \vartheta / \sin^2 \epsilon$ for various settings of the crystal. It is sufficient if this is done for the scattered radiations lying in the plane of incidence. With the aid of the formulæ (6), (7), (9) and (11), it is readily shown that

$$\frac{\sin^2 \vartheta}{\sin^2 \epsilon} = \frac{\sin^2 (\theta + \epsilon)}{\sin^2 \theta_c - 2 \sin \theta_c \sin (\theta + \epsilon) \cos \epsilon + \sin^2 (\theta + \epsilon)} \quad (25)$$

It is seen on differentiating the denominator of the expression on the right-hand side of (25) that it becomes a minimum and the whole expression is therefore a maximum when

$$d \sin (\theta + \phi) = \lambda \cos \phi \quad (26)$$

Equation (26) is equivalent to saying that $1/\Delta$ is then a minimum, as can be seen directly from Fig. 2. The values of $\sin^2 \vartheta / \sin^2 \epsilon$ have been plotted in Fig. 3, as functions of the angle 2ϵ for six settings of the crystal indicated by the

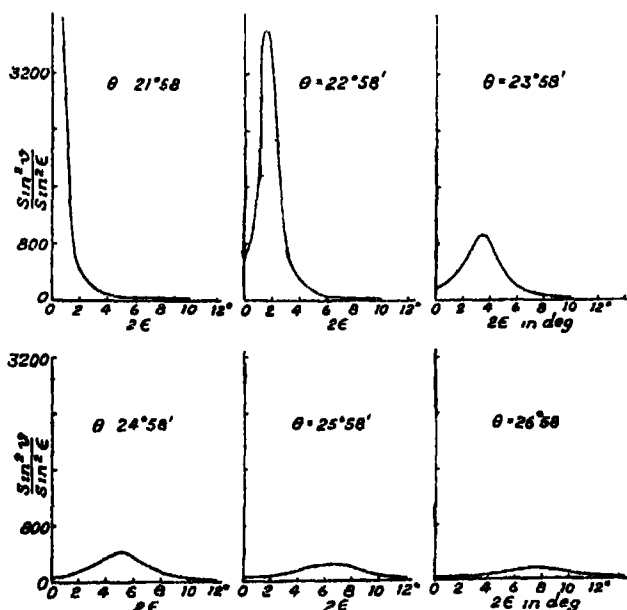


FIG. 3

Graph of the Function $\sin^2 \vartheta / \sin^2 \epsilon$

different glancing angles of incidence θ entered in the figures. The particular case chosen is one in which $\theta_c = 21^\circ 58'$; in the first of the six settings, θ has the value θ_c , and in the others increases by successive steps of one degree.

It will be seen that the peak of intensity which appears in the first setting coinciding with the classical reflection rapidly falls off and is replaced by a relatively weak hump in the curve which spreads over many degrees of arc. The actual value of the numerical factor $\sin^2\theta/\sin^2\epsilon$ also falls off rapidly and becomes insignificant as the crystal is turned away from the correct setting for a classical reflection

We have in the foregoing analysis tacitly made certain simplifying assumptions, viz, that there is only one kind of elastic waves to be considered, that the velocity of the waves is a constant and that the atomic displacements due to the waves are in every case normal to the crystal planes. In reality, there are three sets of elastic waves possible, their velocity is a function of the direction of travel of the waves, and the directions of the displacement are different for the three sets of waves. It should be remembered, however, that the three sets of waves would not all be equally effective in varying the structure amplitudes of the lattice planes. A movement of the atoms parallel to the lattice planes would have no X-ray effect and we may therefore exclude from consideration the types of waves which give rise to such displacements. Further, only such waves as have their wave-fronts roughly transverse to the lattice planes would produce a scattering of X-rays in directions which are appreciably displaced from the static reflections, and are therefore within the range of observation. It follows that we are principally concerned with distortional waves travelling in directions nearly parallel to the lattice planes under consideration and giving atomic displacements nearly normal to them. Hence, the simplified treatment we have adopted should be a fair approximation to the truth. The variation of the velocity of the elastic waves with the direction of travel may be readily taken account of in our formulæ. In any event, such corrections as may be necessary would not affect the broad result which emerges from the theory, namely that the elastic waves produce only a diffuse scattering of the X-rays with very low intensity and not a geometric reflection of the X-rays in any particular direction.

It may be emphasized that the humps of intensity in the X-ray scattering curves appearing in Fig 3 correspond to the elastic waves of greatest wavelength or lowest frequency operative in such scattering. Indeed, the smaller the angle at which the hump or maximum appears, and the more pronounced it therefore is, the lower would be the frequency of the elastic waves responsible for it. Accordingly, it is sufficient, as we have done, to take the energy of the individual vibrations as KT and to treat the problem classically. *At low temperatures, therefore, these maxima of scattering intensity should*

weaken still further and become altogether negligible. This should be so even for crystals of high elasticity, such as diamond, so long as we are considering the X-ray effects due to the elastic vibrations of lowest frequency for which $h\nu^ < KT$*

7 *Quantum Reflection by Infra-Red Vibrations*

The geometric law of dynamic reflection (10) indicates that when the X-rays are incident on the lattice planes at an appropriate angle, the static and dynamic reflections appear simultaneously and in the same direction. The length of the phase waves Δ of the lattice vibration is then infinite, in other words, the atomic vibrations have everywhere the same phase. To enable us to evaluate the dynamic structure factor, we require to know the geometry of the particular mode of vibration as well as its actual amplitude. The former may be derived from a knowledge of the crystal structure and atomic forces, while the latter is determined by the energy of the vibration. The entire crystal being regarded as a single dynamic unit, the energy associated with a single non-degenerate mode of its vibration would be KT on the basis of classical mechanics or $h\nu^*$ according to quantum mechanics. In considering the infra-red or monochromatic vibrations, however, the crystal must be considered as a system having a great number of identical or nearly identical frequencies. To obtain an idea of the results to be expected in consequence of this fact, we may make the simplifying assumption that all the N frequencies of the system are identical, N being the number of lattice cells in the crystal. It follows that the amplitude of the N modes of vibration should be superposed. Each cell in the lattice would then have energy KT (classical mechanics) or $h\nu^*$ (quantum mechanics). The resulting amplitudes of vibrations would be considerable and the dynamic structure factor would no longer be negligibly small in comparison with the static structure factor. Considering also the identity of the phase of the vibration in the N cells, it follows that it would result in a dynamic X-ray reflection having an intensity proportional to N^2 and comparable with the intensity of the usual static reflections. In the language of quantum mechanics, we may express this by saying that the crystal takes up an energy of vibration $h\nu^*$ from the X-ray photon $h\nu$ which is reflected by the lattice planes with diminished energy $h(\nu - \nu^*)$, but that the probability of such a process occurring is increased N -fold by the fact that all the N cells co-operate, their frequencies, amplitudes and phases of vibration being identical.

On the basis of these ideas, we may evaluate the structure factor for a dynamic reflection when it appears in the same direction as a possible static reflection. Denoting by m_p the mass of the p th atom in the unit cell

and by ξ_p its displacement from the position of equilibrium, the energy of a vibration of frequency ν^* may be written as

$$\sum_p 2 m_p \xi_p^2 \pi^2 \nu^{*2} = h \nu^* \quad (27)$$

From this we have

$$\sum \frac{1}{2} m_p \xi_p^2 = \frac{h}{4 \pi^2 \nu^*} \quad (28)$$

If the geometry of the vibration is known, we may evaluate the ξ_p 's from (28) Resolving each ξ_p in a direction normal to the chosen crystal planes, we obtain its component α_p and thence also ζ_p which appears in the dynamic structure factor The latter may thus be determined for any particular mode of vibration and for the particular set of crystal planes A similar procedure would have to be followed if we wish to consider any other possible mode of infra-red vibration or any other set of lattice planes. Taking $h = 6.55 \times 10^{-27}$ erg sec and with $m_p = 40 \times 10^{-24}$ gm and $\nu^* = 6 \times 10^{12}$ sec⁻¹ as representative values, the quantity $\sqrt{h/4\pi^2 m_p \nu^*}$ comes out as a length of the order 0.1 A.U. The ratio of $J_1(\zeta_p)$ and $J_0(\zeta_p)$ appearing respectively in the expressions for the dynamic and static factor is then of the order 1/20 for an average crystal *In other words, under the most favourable conditions, the quantum or modified reflections have intensities which are of the same order of magnitude as the classical or unmodified reflections though, as a rule, definitely weaker*

It is worthy of remark that if a crystal has several possible infra-red modes of vibration, those of the lowest frequencies would in general, as indicated by (28), produce the most important X-ray effects The special importance of the modes of lower frequency would however be less marked on the quantum theory than on the classical mechanics; this becomes evident on writing KT instead of $h\nu^*$ on the right-hand side of (27) We would then have ν^{*2} instead of ν^* in the denominator of (28) The question as to which of the possible infra-red modes is most effective is, however, not so summarily to be disposed of Actually, each set of crystal planes would have to be considered separately in relation to the various possible modes of vibration in the lattice It may well happen that the dynamic structure amplitude of a particular set of crystal planes is largely derived from one of the possible modes of vibration, while another set of planes is chiefly influenced by some other mode It may also well happen that the dynamic structure factors determined by the aggregate effect of all the possible modes of vibration are widely different for different sets of crystal planes and bear no simple relation to the static structure factors of the same

planes Such special features would be characteristic of the individual crystal structure and of the particular modes of its infra-red vibration

The simplifying assumption made above that all the N modes of vibration of the lattice have an identical frequency is equivalent to stating that the only possible phase wave-length is the largest possible, viz, $\Delta = \infty$ This is evidently an extreme assumption, and it would be more reasonable to expect that while the great majority of the possible modes of vibration correspond to a very great phase wave-length, the remainder correspond to lesser values of Δ , thus enabling the dynamic reflections to appear at other settings of the crystal as indicated by equation (10) It would then follow that the intensity of the dynamic reflections should diminish rapidly as the crystal is moved away from the setting at which the static and dynamic reflections appear superposed The fall in intensity would, in fact, represent the distribution of the possible modes of vibration in respect of phase wave-length

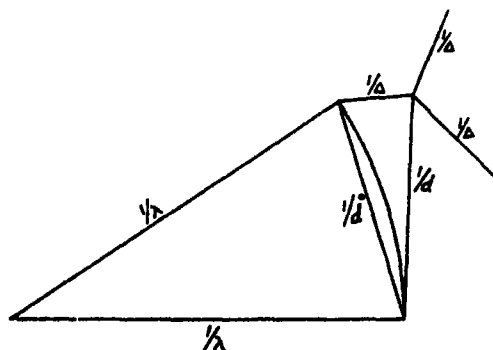


FIG 4
Geometry of Quantum Reflection

The situation indicated above is indicated graphically in Fig 4 The reciprocal of the phase wave-length, namely $1/\Delta$, which we may denote by δ is represented as a vector drawn from the terminus of the vector $1/d$ which gives the spacing and setting of the crystal planes The great majority of the possible values of δ congregate at the origin $\delta = 0$ There are, however, some which spread out along the lines representing the permitted directions of the phase-wave normal. The quantum reflections would then appear at the point or points on the sphere of reflection at which the vectors δ thus drawn meet the latter. As already explained, the dynamic reflections need not necessarily lie in the plane of incidence. The restriction of the vector δ to fall in specific directions differentiates our present case (Fig. 4) from that of quantum scattering also represented geometrically

in Fig. 2. Such a restriction arises naturally from the fact that we are now concerned, *not* with a displacement of the lattice cell as a whole in some *arbitrary direction*, but with a *specific* mode of vibration of the atomic grouping within the cell. The symmetry of such atomic grouping, the nature and magnitude of the inter-atomic forces and especially the geometrical characters of the particular mode of vibration necessarily determine the possible orientations of the phase-vector δ . In the ideal case, therefore, we may expect this to lie in one or another of certain *precisely* defined directions related to the symmetry of the crystal and the symmetry of the mode of vibration. The quantum reflection would then appear, as indicated in Fig. 4, in a *sharply defined* direction (or in sharply defined directions, if, for instance, considerations of symmetry require that there should be several possible directions of the vector δ). It is evident that such a restriction of the phase-vector δ to specific directions would result in a very great increase in the intensity of the observable effects, in fact, the sharper the reflection, the more intense it would be and therefore the more easily observed. Thus, even if only a small fraction of the total number N of possible modes of vibration appear as stragglers from the point $\delta = 0$, their restriction to specific directions of δ should enormously increase the visibility of their effects.

We cannot however always expect the dynamic reflections to exhibit the same sharpness and precisely defined geometric character as the static reflections by the crystal planes. When, for instance, the effects of different possible modes of vibration are superposed, or when the binding forces in the crystal are relatively weak and are further disturbed by thermal agitation, a certain lack of precision in the direction of the phase-vectors would be inevitable. In such a case, the quantum reflections would necessarily be a little diffuse. Since, however, the majority of values of the vector δ congregate at the point $\delta = 0$, all the possible directions of the vector must necessarily crowd together as we approach the common origin. Hence, the reflections should appear not only more intense but also more sharply defined as the crystal setting approaches the position in which the static and dynamic reflections coincide. The same considerations indicate that at the lowest possible temperatures when the disturbing influence of thermal agitation is removed, the diffuseness, if any, of the quantum reflections arising from its presence should diminish and disappear.

As indicated in earlier discussions, the distribution of the N possible modes of vibration amongst various values of the phase-wave vector δ is closely connected with the perfection of the monochromatism of the vibration

frequency The distribution should, in fact, run parallel to the distribution of the N modes amongst the various possible frequencies of vibration The fine structure of the spectral lines in the infra-red region should thus stand in the closest relation to the variation in intensity of the quantum X-ray reflections with the crystal setting It is known from studies on light scattering that the spectral lines representing the lattice vibrations, especially those of the lowest frequencies, become sharper at low temperatures This effect is presumably due to the removal of the thermal agitation which disturbs the precisely defined geometric character of the infra-red vibrations and therefore also their monochromatism Observations at low temperature should thus indicate a closer approach of the X-ray effects towards the ideal behaviour, viz, the appearance of sharply defined and correspondingly more intense dynamic reflections Whether temperature directly affects the distribution of the N possible modes in the δ diagram, in other words tends to transfer a larger proportion of the modes to the origin $\delta = 0$, thereby diminishing the number of stragglers must, for the present remain, an open question It can only be answered when we are in a position quantitatively to formulate the distribution law The strength of the inter-atomic bindings within the lattice cell, and the strength of the forces which link the lattice cells to each other and make the whole crystal a coherent solid must necessarily enter into such a distribution law Only in the ideal case when the lattice cells are firmly linked with each other and the influence of thermal agitation is negligible would be the assumption that the atoms within the lattice cells all vibrate together with identical frequency, amplitude, and phase approach towards the complete truth It follows that our calculation of the intensity of the quantum reflection from equations (27) and (28) should be regarded as setting an upper limit to the intensity of such reflections which would be approached only in the most favourable cases

8 Temperature Factor for Quantum Reflections

The quantum theory of radiation is an application of quantum mechanics to a consideration of the interrelations between matter and radiation In our present problem we are concerned with the effect of passage of a train of waves through a regularly stratified medium in the particular case when the stratifications may, in part, be time-periodic If the existence of such time-periodic stratifications be assumed, classical optics indicates—quite independently of all atomistic or quantum theoretical considerations—that both static and dynamic reflections would be observable under appropriate conditions, the latter appearing with a change of frequency We translate this result into the language of the quantum theory by saying that the

change of frequency arises from the exchange of energy between the photon and the medium, while the optical condition for a dynamic reflection is equivalent to the conservation of momentum in their encounter (Tamm, 1930). Quantum theory indicates that there is a finite probability of a vibration quantum being created or destroyed in the encounter if there be a finite interaction energy between the radiation field and the vibrations of the solid. The fundamentally new feature arising in the quantum mechanics not indicated by the classical or semi-classical theories is that the vibrations, even if non-existent in the absence of the radiation, would be created by it. This is the basis of our equation (27) in which the energy of the oscillation is put equal to $h\nu^*$ and which correctly represents the situation at the lowest temperatures. In the presence of thermal agitation, we have to merely add a contribution due to its effect. In other words, instead of $h\nu^*$ we write the energy of the vibration in equation (27) as

$$h\nu^* \left(1 + \frac{1}{e^{h\nu^*/KT} - 1} \right) \quad (29)$$

The second term within the brackets is the Planck factor. The justification for its inclusion is that the probability of the creation of a vibration quantum would be proportional to the number of such quanta present, and (29) is therefore only valid when we are considering encounters in which the number of vibration quanta is *increased* by the incidence of radiation. In considering the cases in which the number is *diminished*, we must evidently take the energy as

$$h\nu^* \frac{1}{e^{h\nu^*/KT} - 1} \quad (30)$$

In our present problem, the effects of both types of encounters appear superposed, and we may therefore take the energy as the sum of (29) and (30), viz.,

$$h\nu^* \frac{e^{h\nu^*/KT} + 1}{e^{h\nu^*/KT} - 1}. \quad (31)$$

The effect of thermal agitation would be thus to increase the intensity of the quantum reflection or the quantum scattering as the case may be, by the factor

$$\frac{e^{h\nu^*/KT} + 1}{e^{h\nu^*/KT} - 1}, \quad (32)$$

which we shall refer to as the temperature factor in what follows.

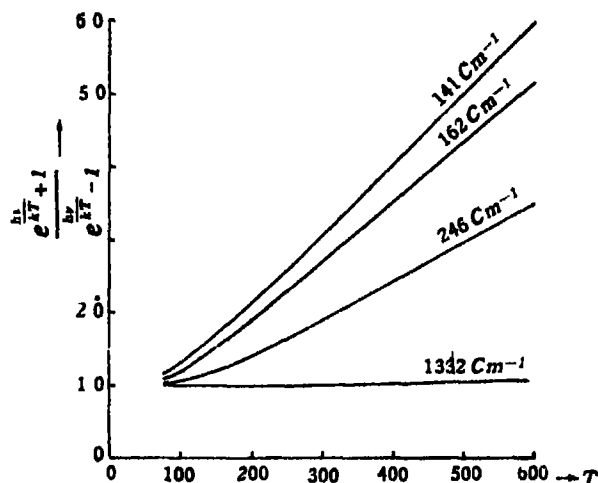


FIG 5

Temperature Factor of Quantum Reflection

In the particular cases when $h\nu^* \gg KT$, viz, when the frequency of vibration is very high or the temperature is very low, the temperature factor reduces to unity and (31) becomes simply $h\nu^*$. On the other hand, when $h\nu^* \ll KT$, viz, when the frequency of vibration is very low or the temperature is very high, the expression (31) reduces to $2KT$. The numerical factor 2 indicates that we are now dealing with the sum of the two effects having the frequencies $(\nu \pm \nu^*)$, whereas previously we are only concerned with $(\nu - \nu^*)$. Thus, at sufficiently high temperatures, the intensities of dynamic reflection and scattering become proportional to the absolute temperature. At what stage this occurs depends on the value of ν^* . To illustrate this feature, the value of the temperature factor has been drawn as a function of the absolute temperature in Fig 5 for a number of different values of ν^* . These are indicated in each case in spectroscopic units against the curves. It will be seen that all the curves tend asymptotically to the value unity at low temperatures. For low values of ν^* , the curve begins to rise steeply at a fairly low temperature, while for high values of ν^* , it remains nearly horizontal over a large range of temperature.

The foregoing is, of course, a simplified treatment, but it is sufficient to indicate the main features of the case. The treatment assumes that the intensity of dynamic reflection is proportional to the energy of the vibration giving rise to it. Such proportionality does not necessarily hold good when the thermal agitation is too violent. It should also be remarked that we are considering the different possible modes of infra-red vibrations as independent

of each other, in other words, we are neglecting their mutual influence. Even when such neglect of the interactions is justified, we must necessarily consider their effects as superposed on each other. When there are several infra-red modes of widely different frequencies, it is possible that the temperature factor may be effectively different for the different sets of lattice planes in the crystal. In other words, those lattice planes whose structure amplitude is noticeably affected by the infra-red vibrations of lowest frequency would show a large temperature factor, while those which are sensibly influenced only by the modes of higher frequency would show a relatively small temperature variation. That such a situation would arise in crystals which are highly anisotropic in structure is extremely probable. That it may occur even in isotropic crystals becomes evident when we recall that the atomic density and the structure amplitude vary enormously for the different planes of a crystal. Some of the planes in a crystal have special properties, *e.g.*, cleavage, determined by the grouping of the atoms and the nature of the atomic bindings. These factors also determine the modes of atomic vibration possible. Hence, it should not be a matter for surprise to find that the temperature factor for dynamic reflection varies greatly for different planes also in isotropic crystals.

9 Temperature Factor for Classical Reflections

We have already noticed in Section 5 that the presence of a vibration which endows the lattice units with a dynamic structure factor simultaneously results in a reduction of the static factor. The reduction arises from the term $J_0(\zeta_p)$ which multiplies the atomic structure factor, this being the same for all the p atoms in the unit cell in the case of an elastic vibration, but different for the p different atoms in the case of an infra-red vibration. The energy of an *individual* vibration being only $h\nu^*$ multiplied by the relevant factors, see (29) and (30), the diminution of the static structure factor produced by it is negligible. The infra-red vibrations, however, have an N -fold degeneracy. The vibration of the atoms resulting from the superposition of the N modes would therefore be sensible and therefore also the diminution of the static structure factor produced by it. When the static reflection appears, the dynamic reflection is also superposed on it and is therefore effectively an addition to its intensity. Nevertheless, if the intensities of the two types of reflection are assumed to be proportional to the squares of their respective structure factors, the diminution of intensity is not compensated by such superposition. In other words, *the possibility of a quantum X-ray reflection by the crystal planes necessarily diminishes the intensity of the classical X-ray reflections by the same planes.*

In practice, there may be several modes of infra-red vibration possible. Their effect and also the *aggregate* effect of the low-frequency elastic vibrations of the lattice on the static structure factor of the atoms requires consideration. We therefore proceed to examine the case in which several different modes of vibrations are superposed. We write for the displacement of the p th atom

$$D_p = d_p + \sum_n a_{pn} \cos(2\pi v_n^* t + z_{pn}) \quad (33)$$

The secondary radiations from the atom have then as their periodic part

$$\cos[2\pi v t - Z_p - \sum_n \zeta_{pn} \cos(2\pi v_n^* t + z_{pn})] \quad (34)$$

The expansion of this in a series of Bessel functions is most easily carried out by writing (34) in an exponential form. It then appears as a product of a series of terms containing v , v_1^* , v_2^* , etc., in the exponentials. On writing out the products after expansion in a series of Bessel functions, we get terms which are periodic in v , $(v \pm v_1^*)$, $(v \pm v_2^*)$, etc., and also periodic terms involving overtones and combinations of v_1^* , v_2^* , etc. Neglecting these latter, the multiplier of the atomic structure factor for the frequency v comes out as

$$\prod_n J_0(\zeta_{pn}) \quad (35)$$

while the multiplier for the atomic structure factor for the frequency $(v \pm v_m^*)$ is

$$J_1(\zeta_{pm}) \prod_{n \neq m} J_0(\zeta_{pn}) \quad (36)$$

For values of ζ which are not too large, we may use the approximation

$$J_0(\zeta) = e^{-\frac{1}{2}\zeta^2} \text{ and } J_1(\zeta) = \frac{1}{2}\zeta \quad (37)$$

Thus, the multiplier for the static structure factor of the atom is

$$e^{-\sum_n \frac{1}{2}\zeta_{pn}^2} \quad (38)$$

the summation in the exponent being over all the n different frequencies of vibration. The multiplier for the dynamic structure factor of the atom for the frequency $(v \pm v_m^*)$ is

$$\frac{1}{2}\zeta_{pm} e^{-\sum_{n \neq m} \frac{1}{2}\zeta_{pn}^2} \quad (39)$$

the summation in the exponent being now made over all the frequencies of vibration except v_m^* . It appears from (38) that all the modes of vibration assist in diminishing the static atomic structure factor, while (39) indicates that the dynamic structure factor for a particular frequency of vibration is

diminished in the same way by all the other modes of vibration. The ratio of (39) to (38) is

$$\frac{1}{2} \zeta_{pm} \cdot e^{-\frac{1}{2} \gamma_{pm}^2} \quad (40)$$

and depends only on the displacements of the atom due to the vibration of frequency ν_m^* . In this particular sense, each different vibration may be regarded as acting independently of all others, in other words as giving a quantum reflection of which the intensity in relation to the classical reflection is determined exclusively by its own amplitude.

In the summation indicated by the exponent in (38), we have to include all the frequencies of vibration of the lattice. We recall that

$$\zeta_{pm} = \frac{4 \pi a_{pm} \sin \theta}{\lambda} \quad (41)$$

where a_{pm} is the displacement of the p th atom resolved normal to the crystal plane due to the vibration of frequency ν_m^* , the actual displacement ξ_{pm} being given by the geometry of the vibration and its energy. Considering the elastic vibrations first, we have already noticed that those of the lowest frequencies give the largest atomic displacements. On the other hand, the modes of the higher frequencies are far more numerous. Thus, the entire range of possible frequencies of elastic vibration would contribute towards determining the product (38) which alters the atomic structure factor. The treatment of the problem by Debye, Waller and Laue however greatly exaggerates the part which the elastic vibrations of the lattice play in this respect. Firstly, there is no justification for assigning all the $3Np$ degrees of freedom to the elastic vibrations. The maximum number which can properly be so assigned is $3N$, the remaining $(3p-3)N$ degrees of freedom representing the infra-red or monochromatic vibrations of the lattice. Then again, the actual frequency limit for the elastic spectrum is automatically reduced by the diminution in the number of degrees of freedom allotted to it. Thirdly, the semi-classical way in which the quantum theory of specific heats and the zero point energy are usually brought into the X-ray problem is, of course, invalid. Finally, in the vast majority of actual crystals, the Einstein or monochromatic vibrations, besides being more numerous, have often quite low frequencies and therefore make a notable contribution to the thermal energy. Their influence on the intensity of the classical reflections indicated by (38) should therefore be of great importance, in fact much more so than that of the elastic vibrations of the lattice.

It follows from what has been stated above that there should be a considerable degree of correlation between the intensity of the quantum

reflection by a particular set of crystal planes and the temperature variation of the intensity of the classical reflection by the same set of planes. An intense quantum reflection can only arise if the structure amplitudes are strongly influenced by the possible modes of infra-red vibration with a corresponding diminution of the static structure factor. We should then ordinarily expect a notable temperature effect of the intensity of classical reflection, *pari passu* with an increase of the intensity of quantum reflection with rising temperature. Since however, the static and dynamic structure factors for the unit cell are determined by different considerations, the correlation indicated above is not necessarily to be observed in all cases.

10 Summary

The ideas indicated in the preceding paper are here worked out quantitatively. The secondary radiation from an oscillating atom in a crystal traversed by X-rays is analysed into its frequency components. It is shown that the interferences to which each component of altered frequency gives rise are determined jointly by the positions of the atoms and the phases of their vibration. It follows that besides the static reflections of unmodified frequency by the crystal planes, we would also have dynamic reflections of altered frequency. The geometric law of such dynamic reflection is derived. The static and dynamic structure factors are deduced and it is pointed out that the elastic and infra-red vibrations of the lattice stand on a different footing in respect of these factors. Considering first the elastic vibrations, formulæ are obtained and graphs are drawn which show that such vibrations give rise to a diffuse scattering of the X-rays with low intensity proportional to the number of lattice cells. The N -fold degeneracy of the monochromatic infra-red vibrations, on the other hand, results in their giving true geometric reflections with altered frequency and with intensity proportional to the square of the number of lattice cells. The intensity of such reflection is evaluated on the basis of the quantum theory of radiation. The variation of the intensity, direction and sharpness of the quantum reflections with crystal setting is discussed. A formula is then obtained for the temperature variation of the intensity of the quantum reflections. The temperature factor for the intensity of the classical reflection is also written down and the extents to which the elastic and infra-red vibrations respectively contribute to it are discussed.

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QUANTUM THEORY OF X-RAY REFLECTION: EXPERIMENTAL CONFIRMATION

BY SIR C V RAMAN AND DR P NILAKANTAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE fundamental discovery that the lattice planes in a crystal give rise to monochromatic X-ray reflections of a second kind involving a change of frequency was made in the laboratories of this Institute and announced at the Easter meeting of the scientific societies of Bangalore held on the 22nd March 1940. It was an essential part of the discovery that the experimental characters of the phenomenon as actually observed were such as to place it entirely outside the range of the accepted theories in X-ray optics. The explanation of the newly discovered phenomena, in fact, demanded the introduction of radically new ideas regarding the nature of the vibrations possible in crystal lattices and also regarding the nature of the interactions which occur when X-rays traverse a crystal. These new ideas were indicated simultaneously with the new experimental facts in an article in *Current Science* for April 1940. Though new to X-ray physics, the ideas set out in that article had already emerged more or less clearly from the spectroscopic investigations on the scattering of light in crystals which had previously been engaging the attention of the laboratory*. The application of these ideas in the field of

* A brief summary of these investigations and the ideas emerging therefrom will be found in the Franklin Medal Day lecture to be published in the *Franklin Institute Journal* for September 1941

X-ray research was thus almost inevitable. The further investigations which have since been continued systematically at this Institute have not merely confirmed the statements made in the first publication, but have also shown that the new X-ray results taken together with the earlier spectroscopic studies compel revolutionary changes in our concepts of the solid state. In fact, the X-rays directly demonstrate what had been previously only inferred from the optical evidence, namely, that the lattice vibrations appearing as monochromatic lines in the spectrum of a crystal possess a degree of orderliness and coherence which is astonishing and truly as remarkable as the orderliness of the static arrangement of the atoms characteristic of a crystal. The optical and X-ray methods of investigating the lattice vibrations in crystals thus stand in the closest relation, supplementing each other. The optical methods enable us to analyse the infra-red vibrations into their frequency spectrum and only indirectly to infer their geometric character. The X-rays, on the other hand, enable us directly to ascertain the geometrical characters of the vibration and only indirectly to infer the frequency changes involved.

The clear-cut enunciation of the new facts and ideas put forward in April 1940 was made possible largely by the deliberate choice of diamond as the crystal round which the investigations have principally centred. The known perfection of this crystal, the simplicity of its structure, the possibility of using relatively soft X-rays in working with it, and above all, the geometric precision with which it exhibits the new phenomena have enabled the latter to be understood much more clearly than would have been otherwise possible. For this reason, the present article will be devoted wholly to the results of the experimental studies made with diamond. It will be shown, on the one hand, how the experimental facts totally exclude any explanation of the type based on the original theories of Debye, Waller and Faxén, with or without such further modifications as have been recently suggested. It will, on the other hand, be shown how completely the experimental facts fit into the scheme of new ideas expounded and developed quantitatively in the two preceding papers. It must not be imagined however that the case for the new theory rests exclusively on the facts observed with diamond. So far from this being the case, it may be said that a careful and unprejudiced examination of the facts with any crystal is sufficient to show that the efforts recently made by several workers, notably Zachariasen, Max Born and the group at the Royal Institution to base an explanation of the new X-ray facts observed at this Institute on the basis of the existing theories or modifications thereof are not on the right lines. In the earlier paper on basic ideas, the effects indicated by the theories of the Debye type are set out and contrasted with those indicated by the quantum theory of X-ray reflection, and a series of experimental

criteria are put forward enabling a discrimination between the two. In the papers which follow in these *Proceedings*, these criteria have been applied in several cases, and in every case the verdict of the facts has been in favour of the new ideas. Equally striking has been the success of the new ideas in dealing with problems of the solid state which have hitherto proved baffling, e g, the large deviations of the observed specific heats of elementary solids, such as metals, from those indicated by the Debye specific heat formula. Far from such a failure of the Debye theory being surprising, it is a necessary consequence of the idea that the lattice spectrum of every crystal includes Einstein or monochromatic frequencies of vibration. Mr Bisheswar Dayal has shown in a series of papers which will appear in the next issue of these *Proceedings* that the specific heat curves for metals and other elementary solids find a very simple and complete examination on the basis of these new concepts in crystal dynamics.

2 *Structure and Lattice Spectrum of Diamond*

The specific heat of diamond has been accurately measured by Pitzer (1938) over the range of temperature from 70° T to 288° T . His data do not fit into the Debye formula, showing deviations as large as fifteen per cent within this range, if the limiting frequency in the formula is chosen to fit the data at the lower limit of temperature. The cause of this failure becomes apparent when we consider the real nature of the lattice spectrum. The Debye theory of specific heats rests on the belief that the infra-red vibrations of the lattice are physically of the same nature as the vibrations of the acoustic type and form a continuous spectrum of frequencies. That the same idea forms the basis of the crystal dynamics of Max Born and his school is evident from the postulate of the "cyclic lattice" on which the work of that school rests and which has been discussed earlier in these *Proceedings* and shown to be untenable. The Born postulate places the elastic and infra-red vibrations mathematically on the same footing. Its implications become clear when we examine the results of the calculations worked out on its basis by Blackmann, Kellerman and others of that school. The calculations lead to representations of the vibration spectrum which while differing in detail from that assumed in the Debye theory, have nevertheless the same fundamental feature, namely that the vibrations of the extended solid forms a continuous spectrum of frequencies. The lattice spectra of actual crystals as revealed to us by spectroscopic investigations, especially those made at low temperatures, present us with a totally different picture. Indeed, it may be said that the assumptions made in the Debye theory and in the Born crystal dynamics bear no resemblance whatever to the actual facts at such temperatures.

Several different lines of investigation agree in showing that, except possibly in the region of the lowest frequencies where the experimental techniques have not at present been good enough to give a definite answer, the lattice spectrum of diamond consists of sharply defined or monochromatic frequencies. Bhagavantam (1930) investigated the scattering of light in diamond and found numerous sharp lines in the spectrum giving the following frequency shifts in wave numbers per centimetre 1585, 1480, 1431, 1382, 1332, 1288 and 1158. Amongst these, the 1332 line is at least a hundred times more intense than the next most intense line 1158, while the others were just detectable in the spectrum of a large clear white diamond. The 1332 line, besides being intense, is also extraordinarily sharp, in fact exactly as sharp as the exciting radiations. It remains sharp (though with gradually diminishing frequency shift) over the whole range of temperature from 93° T. to 1130° T. Further evidence on the lattice spectrum of diamond has been furnished by the recent investigations of Nayar at this Institute on its luminescence and ultra-violet absorption spectra at low temperatures. As was first noticed by Ramaswamy, diamond exhibits a fluorescent band at 4157 Å U, the same band also appearing in absorption. On cooling down the crystal to liquid-air temperatures, this band shifts to 4152 Å U, at the same time becoming much sharper. Subsidiary bands are also noticed at lower frequencies in fluorescence and at higher frequencies in absorption, the frequency differences between these and the 4152 band being the same but of opposite sign in fluorescence and in absorption. These frequency differences therefore represent the lattice spectrum of diamond. The band at 4152 Å U is not as sharp at liquid-air temperature as could be desired, and it is greatly to be hoped that this work will be repeated at liquid hydrogen temperatures in some cryogenic laboratory. Nevertheless even at liquid-air temperatures and using the fairly high dispersion provided by an E_1 Hilger spectrograph, Nayar has found that the fluorescence and absorption bands appear resolved into numerous *discrete frequencies*. These are (within about ten wave numbers) 1341, 1252, 1148, 1090, 1010, 960, 784, 681 and 532. There are indications of larger frequency shifts in the same region as those observed by Bhagavantam, as also of several discrete frequency shifts smaller than 532 appearing very feebly in the spectra. Plate XVI, Figs 4 (a), (b) and (c) reproduce the lattice spectrum of diamond as observed respectively in light-scattering, in fluorescence and in absorption, and exhibit these frequency shifts.

The dynamical theory of the diamond lattice has not at present been worked out with sufficient thoroughness to enable us to explain all these

experimental results It is noticed, however, that the most intense fluorescence and absorption frequencies fall roughly into two groups. The head of one of these groups is close to the 1332 frequency which appears as an extremely intense and sharp line in light scattering. The nature of the 1332 vibration has been very fully discussed by Nagendra Nath (1934) and was indicated by him as an oscillation relative to each other of the two Bravais lattices of carbon atoms which constitute diamond. Since each carbon atom belonging to one lattice is bound by valence bonds to four carbon atoms in the other lattice, and *vice versa*, such an oscillation would necessarily have a high frequency. Indeed, a calculation based on the known force constants gives a frequency in fair agreement with the observed 1332. The symmetry characters of such an oscillation (Venkatarayudu, 1938) also indicate that it should be active in light-scattering. The identification of the 1332 frequency as that of an oscillation of the two interpenetrating lattices of carbon atoms relative to each other is thus firmly established. The second group of frequencies of which the head is at 784 is completely inactive in light scattering. It is therefore very probable that the oscillations of this group involve movements of the atoms in each Bravais lattice against themselves, alterations of the tetrahedral valence angles rather than the extensions or compressions of the valence bonds determining the observed frequencies.

Examining the structure of diamond, we find that the carbon atoms belonging to the two Bravais lattices appear in the planes parallel to the octahedral faces in separate layers which are alternately at *unequal distances*. It follows from this fact and the considerations set out in the preceding paper that the (111) planes would have their structure amplitudes strongly varied by the 1332 oscillation. A similar situation would also arise in respect of any oscillation in which the movements of some of the atoms in one Bravais lattice are balanced by opposite movements of an equal number of atoms in the other lattice. If, on the other hand, we consider a type of vibration in which the movements of the atoms in one lattice are balanced by opposite movements of the remainder of the atoms in the same lattice, it is easily seen that the structure amplitudes of the octahedral planes would remain unaffected. It is thus evident that only the 1332 vibrations or other vibrations of similar character would influence the structure amplitudes of these planes. A simple calculation on the basis of the theory set out in the preceding paper shows that in spite of the high frequency involved in such oscillations, dynamic reflections of notable intensity should be given by the (111) planes. On account of the high frequency of the associated vibrations of the lattice, such reflections should be practically insensitive to variations of temperature.

The crystal spacings in diamond giving the classical X-ray reflections are of two kinds. In one set which includes the spacings parallel to the octahedral faces, the alternate layers of carbon atoms appear unequally spaced in the ratio of 1 3. In the second set, which includes the planes parallel to the forms of the cube and the dodecahedron, the planes appear equally spaced. In the planes parallel to the dodecahedral faces, the carbon atoms belonging to the two Bravais lattices appear interspersed with each other in equal numbers. It follows that these planes are incapable of giving a dynamic reflection as a result of the relative oscillation of these two lattices. This conclusion, however, only refers to this particular mode of vibration having the high frequency of 1332 wave-members. There are numerous other modes of vibration of the lattice with discrete frequencies, some of which are as low as 127, 178, 303 and 421 wave-numbers (Nayar, 1941). In such vibrations, there can be no doubt that the atoms in each Bravais lattice oscillate against each other, that is, some of the atoms move one way and the others move the opposite way to balance the oscillation. The extreme feebleness with which the frequencies lower than 532 appear in fluorescence and absorption probably indicates that such vibrations have a relatively small *a priori* probability. Nevertheless, a low frequency involves a correspondingly larger amplitude of vibration. Hence, the planes in the crystal which cannot give a dynamic reflection associated with the 1332 vibration may nevertheless give observable reflections associated with some of the vibrations of the lattice with lower frequencies. Such reflections would be indicated by their intensity being more temperature-sensitive than the reflections associated with the high-frequency vibrations.

3. Specular Character of Quantum Reflections

Amongst the many items of supporting experimental evidence set out in the publications by the present writers (1940) announcing the discovery of quantum or modified reflection, one of the most cogent which was duly emphasized was the truly geometric or specular character of the reflections associated with the (111) planes of diamond. This feature by itself and apart from all other evidence was sufficient proof that the phenomena described in those papers lay entirely outside the scope of X-ray optics as it existed before the announcement of the discovery. In view of the importance of this feature and especially of the fact that it is absolutely fatal to the attempts made by Max Born and others to interpret the phenomena on the basis of the Debye-Born crystal dynamics, we shall here consider it in some detail.

Even in the photographs published with our earliest communications (*Current Science*, April 1940 and *Nature*, 27th April 1940), it was evident

that the quantum or dynamic reflections given by the (111) planes of diamond were just as sharp as the ordinary Laue reflections by the same planes. While the Laue reflections appeared as elliptic spots, the quantum reflections were round in shape and had about the same diameter as the major axis of the Laue spots. These features are readily understood when the angular divergence of the incident beam is considered and it is borne in mind that a quantum reflection can occur at any incidence of the X-rays on the crystal planes. A detailed discussion of the geometric aspects of the quantum X-ray reflections in diamond by Mr P. R. Pisharoty has already appeared in a recent issue of these *Proceedings* (1941). Mr Pisharoty has proved that the appearance of the quantum reflections as observed in the photographs for all possible settings of the crystal is just what we should expect if they were perfectly geometric.

In actual experimental work with X-rays, the radiation from the source is necessarily divergent. The extent and manner in which such divergence may be advantageously limited depends both on the aim of the investigation as well as upon the material under study, viz., upon the thickness or area of the crystal. In investigating phenomena of low intensity, an undue restriction of the divergence of the beam would merely increase the difficulties of the investigation without advancing its purposes in any way. Thus, for instance, in the present problem, when we wish to decide whether we are dealing with a sharp reflection or a diffuse scattering, instead of reducing the aperture excessively, it is preferable to retain it at a reasonable value and prolong the photographic exposures as much as possible. In such circumstances, a geometric reflection would not enlarge in area, while a diffuse scattering would progressively widen out. Using the technique here indicated, it is easy to decide the question whether the quantum reflections in diamond enlarge their angular extension when the crystal is moved away from the setting at which the quantum and classical reflections coincide. By not reducing the width of the X-ray beam unduly, it is possible to record the spots with fair intensity even when the crystal setting is altered by as much as 6° in either direction. It will be seen from the photographs reproduced in Plate XVII, Figs 5 (a) to (k) that the extension of the quantum reflections remains constant over this whole range of settings, while if it were due to a scattering of the X-rays associated with the reflections of the usual kind, it should enlarge rapidly in area. One has only to glance at the photographs in Fig. 5 and then turn to the set of curves reproduced in Fig. 3 of the preceding paper showing how the distribution of intensity of scattering of X-rays varies with the setting of the crystal to realise the futility of any attempt to explain the actual phenomena in terms of the scattering theory.

The classical and quantum reflections have a different origin and obey different geometric laws. Nevertheless, they are both geometric reflections, and optical principles indicate various simple criteria which can be employed to test their nature as such and which would reveal the correct position immediately if the quantum reflection were not an independent phenomenon. Various factors in the experimental technique are capable of variation, *e.g.*, the area and angular divergence of the incident X-ray beam, as well as the area and the thickness of the crystal irradiated by it. These variations would influence the intensity and the angular spread of the two effects in a very different manner if they were not essentially similar phenomena. Actually, we observe a complete parallelism in the behaviour of the classical and quantum reflections when the experimental factors are varied separately or together. It is well known, for instance, that the spots in a Laue pattern diminish in extension when the X-ray beam is made narrower, and that such diminution in size cannot be prevented from occurring by merely prolonging the photographic exposures. Precisely the same effect is observed with the quantum reflections by the (111) planes in diamond. These are reduced in extension by limiting the area of the X-ray pencil in much the same way and in the same proportion as the ordinary Laue reflections, longer exposures not altering the situation. It is also noticed that the relative intensity of the Laue and quantum reflections remains unaltered by such procedure, thus proving that we are dealing with true geometric reflections in both cases and not a reflection in one case and a scattering in the other.

The classical X-ray reflections by the lattice planes of crystals appear in directions which are geometrically definable with a degree of precision depending on the perfection of the crystal. Diamond, for instance, may be so perfect that the setting at which it reflects monochromatic rays with the maximum intensity is probably definable with as great an accuracy as the wave-length can itself be specified. In the case of the quantum reflection, we are concerned not only with the geometric perfection of the crystal but also with its *spectroscopic* perfection, that is to say, with the monochromatism of the infra-red vibrations of its lattice. As will be seen from Fig. 4 (a) in Plate XVI, the monochromatism of the 1332 vibration of the diamond lattice, even at ordinary temperature, is of the most remarkable kind. Accordingly, we should expect that the quantum reflections by the (111) planes which owe their origin to it should have a precisely definable geometric character and should be unaffected in their sharpness by the setting of the crystal. A rigorous test of this question is not so easy as in the case of the classical reflections, for the quantum reflections can occur independently of the angle of incidence of the X-rays on the crystal.

Hence, an angular divergence of the incident beam and therefore also of the reflections can easily be mistaken as indicating a lack of geometric perfection of the latter. The severity of the test which can be made depends on the possibility of obtaining an X-ray beam with small lateral extension and angular divergence but of sufficient intensity to record the quantum reflections in a reasonable time. As the intensity of the reflections falls off with extreme rapidity when the crystal setting is turned away so as to separate the classical and quantum reflections, it is evidently not easy to push the question to the final limit. It may be stated, however, that, *the quantum reflections by the (111) planes of diamond are geometrically as perfect as can be experimentally ascertained at the present time*. This is shown by the photographs reproduced by Figs 6 (a) and (b) in Plate XVIII. In these photographs, the quantum reflections by the (111) planes have been recorded using a fine rectangular slit 100 millimetres deep and 0.15 millimetre wide, and a cleavage plate of diamond 0.76 millimetre thick. The width of the reflections as measured on the plates is no greater than that to be expected from the finite lateral extension of the beam, its angular divergence and the thickness of the plate used. It is specially noteworthy that the reflection as recorded on the plates shows no detectable widening when the crystal setting is altered so as to make the quantum reflection move away from the Laue reflection in one direction or the other by several degrees.

These facts show that there is no ground for the belief entertained by some X-ray workers in the Debye-Waller-Faxén theory of X-ray scattering as a possible explanation for the phenomena discovered with diamond at this Institute. So striking are the facts that even the advocates of the scattering theory have been compelled to take the illogical step of referring to the phenomena as a "diffuse reflection" instead of as a "diffuse scattering" which would be the correct nomenclature for them to adopt on the basis of that theory. Indeed, the designation of "diffuse reflection" as applied to the case of the (111) quantum reflection of diamond is quite misleading. Actually, these reflections are probably as sharp or sharper than the classical reflections of X-rays by the lattice planes of many crystals of the ordinary or imperfect type.

4 Geometric Law of Quantum Reflection

Any discussion regarding the geometric law of the quantum reflection presupposes its specular character. Indeed, unless we are dealing with a phenomenon which is recognizable as a reflection over a wide range of settings of the crystal and whose position can be observed and stated with some precision, there can be no point in discussing the validity of any geometric formula

descriptive of it. No useful purpose would be served, for instance, in seeking to find empirically the point of maximum intensity in a field of diffuse scattering such as those represented theoretically in the curves of Fig. 3 of the preceding paper. The precision with which the positions of the X-ray reflections can actually be located and measured is an indication that the experimental situation in this respect is very different indeed from that arising in the case of X-ray scattering.

The earliest measurements made with diamond (Raman and Nilakantan, May 1940) showed that the spacing d^* of the dynamic stratifications altered rapidly with the setting of the crystal, being identical with the static spacing d of the (111) planes only at the particular setting when the two types of reflections appear superposed. It was found later that even these early measurements fitted perfectly into the general geometric law of quantum reflection

$$2 d \sin \psi \sin (\vartheta + \epsilon) = \lambda \sin \vartheta, \quad (1)$$

the angle ϑ coming out the same within a degree or two as the value of $54^\circ 44'$ established by the measurements over a wider range of settings of the crystal made in July and August 1940. The angle $54^\circ 44'$ is half the tetrahedral angle between the valence bonds joining the carbon atoms in diamond. It is also the angle between the faces of the cube and the octahedron in the regular crystal system. In other words, *the phase-waves for the quantum reflection of X-rays by the octahedral planes of diamond are parallel to the cube faces of the crystal*. This remarkable result which was discovered experimentally in September 1940 forms a striking confirmation of the basic ideas underlying the quantum theory of X-ray reflection. It emerged from the extended studies made in the preceding months as mentioned above. The photographs from which the measurements were made are reproduced in Plate XVII, Figs. 5 (a) to (k). A brief reference to this result was made in a footnote to the paper by Raman and Nath (November 1940) in which the theoretical formula (1) was first announced. The result itself was communicated in a letter to *Nature* dated the 11th November 1940 and published in its issue of the 25th January 1941. In view of the great significance and importance of the result, it appears worth while to give a detailed account of the experimental work which led to its recognition.

These early experiments were carried out with a 'Spektro Analyt' Rontgen apparatus manufactured by Siefert & Co., Hamburg. The X-ray tube was of the sealed hot-cathode type with a copper target, the X-rays emerging through four windows of Lindemann glass. The tubes worked at 41,000 k v., with a tube current of 12 ma. A flat film type of camera was employed for taking the photographs. The X-ray beam was restricted by a

circular hole bored through cylindrical lead blocks of effective depth 93 mm , the diameter of the hole being 1.6 mm

Diamond has a perfect cleavage parallel to an octahedral face of the cubic crystal. Plates evidently obtained by cleavage in this manner and subsequently polished can be readily obtained from jewellers in India. The plate actually used was about half a square centimetre in area with a thickness of 0.76 millimetre. The crystal was mounted on the goniometer with its faces nearly vertical and nearly normal to the X-ray beam. The crystal was set by trial so that the (111) planes within the crystal from which the reflections were to be studied were vertical, as also the adjoining lattice spacings parallel to the form of the cube. Thus, when the crystal was rotated about the vertical axis of the goniometer, the plane of incidence of the X-rays on the (111) spacings remained horizontal throughout, coinciding with a plane of symmetry of the crystal parallel to the form of the dodecahedron. Particular care was taken in mounting the crystal to ensure that the goniometer axis passed through the portion of the crystal irradiated by the X-ray beam. Small rotations of the crystal introduced no sensible change in the distance from the crystal to the photographic film. This however, was checked up at every setting of the crystal. The actual distance from the diamond to the film was 3.99 centimetres for Figs 5 (a) to (g) and 3.95 cm for Figs 5 (h) to (k) in Plate XVII. With the aperture used, the X-ray beam traversing the diamond had an appreciable angular divergence. The round shape and sharpness of the spot as recorded on the film, however, enabled the position of its centre to be located with such accuracy that the use of a finer X-ray pencil would merely have prolonged the exposures necessary and thereby increased the difficulties of the investigation without any material gain in precision.

Since, in these experiments, the reflections occur in a plane of symmetry of the crystal, it follows that we may write the geometric law (1) in the form

$$2d \sin \frac{1}{2}(\theta + \phi) \sin \left(\delta + \frac{\theta - \phi}{2} \right) = \lambda \sin \delta \quad (2)$$

θ and ϕ being the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Since the actual value of the crystal spacing is known, viz., 2.056 Å, the most convenient representation of the data is to regard the spacing as an unknown function of θ to be determined from the observed values of θ and ϕ and the formulæ used. The angle δ disappears from equation (2) when $\theta = \phi$. Thus, whatever be the chosen value of δ , the graphs representing the calculated values of the spacing as a function of θ calculated with different assumed values of δ all necessarily cross at the same point. This should agree with the known spacing of the crystal.

within the limits of experimental error. When however, $\theta \neq \phi$, the spacing calculated would diverge progressively from the actual value unless the correct value of ϕ has been chosen. The appearance of the graph as a horizontal line in a position agreeing with the known crystal spacing thus furnishes an exact test of the formula employed.

Fig 1 shows three graphs in which the experimental observations have been set out in the manner indicated. The graphs marked d_1 represents the

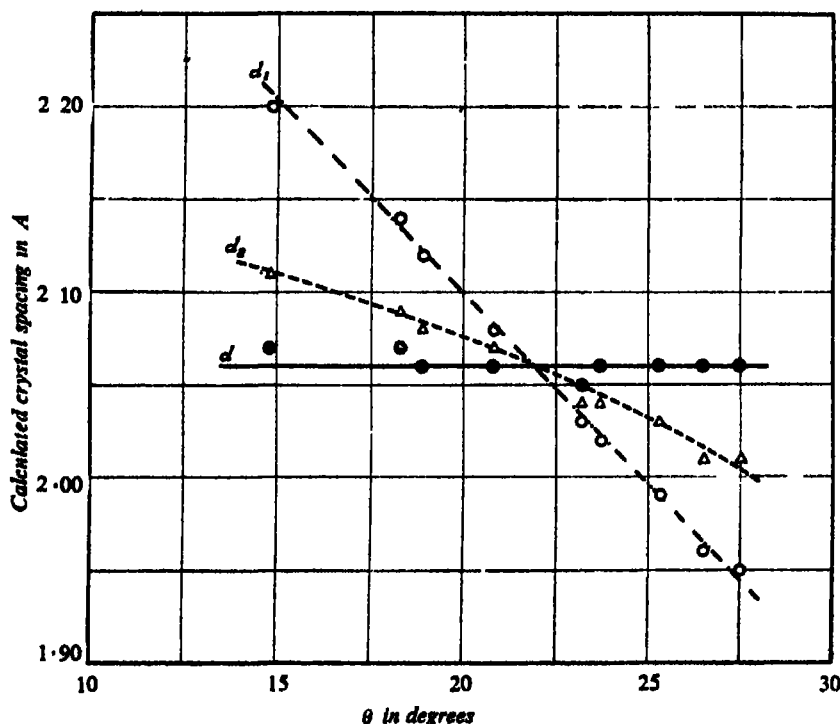


FIG 1 Geometric Law of Quantum Reflection

crystal spacings calculated from the approximate formula

$$2 d \sin \frac{1}{2} (\theta + \phi) = \lambda \quad (3)$$

The graph marked d_2 represents the crystal spacings calculated from the formula

$$d (\sin \theta + \cos \theta \tan \phi) = \lambda. \quad (4)$$

This formula which is of the same form as that derived originally by Faxén on the basis of the scattering theory, would also represent the geometric formula of quantum reflection if the phase-waves of the infra-red lattice vibration had an arbitrary orientation within the crystal, and the actual

geometric position of the reflection were determinable from a consideration of the minimum phase wave-length. The graph marked d in the figure was calculated from the formula (2) above, assuming ϑ to be $54^\circ 44'$. It will be seen that it is a horizontal straight line with a spacing very closely agreeing with the known value. On the other hand, the graphs d_1 and d_2 diverge rapidly from the known spacing at except the point where all the three graphs intersect

To indicate the degree of accuracy with which the angle ϑ is determinable from the observations, the graphs drawn for three different values of the angle are shown in Fig 2. It will be seen that the angle lies certainly within one degree of half the tetrahedral valence angle

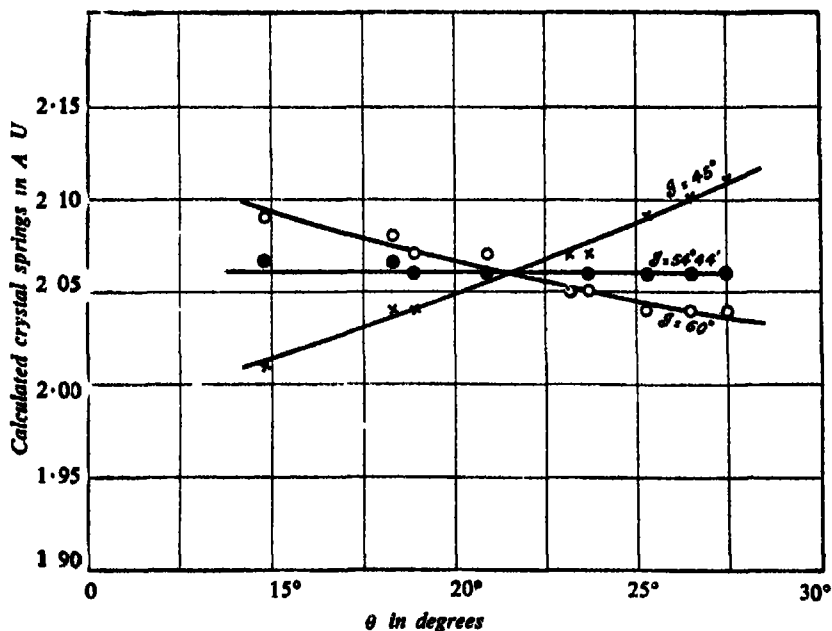


FIG 2. The Inclination of the Phase Waves

The experimental facts emerging from Figs 6 (a) and (b) in Plate XVIII, and from Figs 1 and 2 above in the text are thus of a completely decisive character. The Debye-Faxén-Waller theory of X-ray scattering demands a distribution of the intensity of the scattered X-rays over an area whose angular extension is expressed in as many degrees of arc as the setting of the crystal is moved away from the position required for the classical X-ray reflection. It also demands that the position of maximum intensity in such scattering, though not capable of being measured with any particular precision, should follow the course of the curve marked d , in Fig. 1. On the other hand,

the actual spread of the quantum reflection is not experimentally detectable and if it is finite, is measureable in minutes of arc rather than in degrees, as indicated by Figs 6 (a) and (b). The geometric direction of the reflection is capable of being determined with precision and follows a wholly different law, namely that defined by equation (2) above. The facts thus definitely negative any possibility of explaining the phenomena in terms of the Debye-Faxén-Waller theory. *The observed specificity of the value of θ also forms a direct experimental contradiction of the Born postulate of the cyclic lattice*, since the latter assumes the phase-waves of the vibration of the crystal lattice to have all possible orientations instead of a definitely restricted orientation as shown by the X-ray results. We have thus no choice left except that of assuming the infra-red or high-frequency vibrations of the lattice to be the factor responsible for the observed X-ray reflections.

We may now consider the question why the phase-waves of the 1332 vibration which are evidently responsible for the (111) reflections are parallel to the form of the cube. The answer to this is evidently that the nature of this vibration is determined by the geometry of the crystal structure. Each carbon atom in one Bravais lattice is joined by four valence bonds in a symmetrical fashion to four other carbon atoms belonging to the other Bravais lattice. The individual valence bonds are normal to the octahedral planes in diamond, while the planes parallel to the cube faces bisect the angles between the valence bonds taken in pairs. The vibration responsible for giving the reflection by a particular set of octahedral planes is normal to them and therefore parallel to one of the valence bonds. Since the three other bonds are also possible directions for such a vibration, it is to be expected that the plane of the phase-waves would take an intermediate direction, which by symmetry should bisect the angle between them. On the basis of this argument, it is evident that there should be three sets of possible phase-waves which are respectively parallel to the three pairs of faces parallel to the forms of the cube. This result demanded by considerations of symmetry is found as we shall see presently, to be fully supported by the experimental facts.

5 *The Azimuth Effect*

A further remarkable confirmation is forthcoming for the result that the phase-waves associated with the 1332 vibration are restricted to a specific crystallographic orientation. This is the so-called azimuth effect, which was foreseen theoretically before it was sought for and confirmed experimentally by the authors. Since the phase-waves for a (111) reflection are parallel to the adjoining cube face, it follows that if the crystal plate be rotated in its own plane so as to make the plane of incidence no longer a plane of symmetry of

the crystal, the quantum reflection should move out of such plane of incidence. Why this effect occurs becomes evident when we recall that the plane in which the quantum reflection should appear is the plane of incidence of the X-rays on the dynamic stratifications, in the circumstances considered, these are no longer perpendicular to the plane of incidence of the X-rays on the static crystal planes. This situation is readily appreciated with the aid of a vector diagram in which the reciprocals of the crystal spacing and of the phase-wave normal are geometrically represented. The point at which the phase-wave normal intersects the sphere of reflection necessarily moves out of the plane of incidence when the crystal is rotated in its own plane, the angle of incidence being retained constant. It is evident that such displacement would be zero if the reciprocal phase wave-length is zero; it changes sign when the direction of the wave-normal is reversed either by a change of the crystal setting or by a change of the X-ray wave-length. In other words, the displacement of the quantum reflection out of the plane of incidence would be zero when it coincides with the Laue reflection, and would be of opposite signs when it lies respectively on the two sides of it. It should also increase progressively as the quantum reflection moves away from the Laue spot in either direction. The theory of the effect has been very fully discussed and illustrated by appropriate diagrams in the paper by Pisharoty already cited. We need not therefore enter into the matter here in further detail. The necessary mathematical formulæ will be found in Pisharoty's paper. The effect is illustrated in Figs 10 (a) and (b) in Plate XIX. The angular displacements of the reflections out of the plane of incidence as measured from the photographs are in quantitative agreement with those deduced from the formulæ.

6 *Explanation of Multiple Spots and Streamers*

Another striking confirmation of the theory of phase-waves is afforded by the phenomena arising from the fact that there are three sets of phase-waves and therefore three quantum reflections corresponding to the points where the phase-wave normals meet the sphere of reflection. As these normals are at right angles to each other, it is not to be expected that all the three reflections would be observable in every case. The setting of the crystal would obviously determine the effects actually recorded. It is evident that if the phase-wave vector nearly grazes the sphere of reflection, the finite divergence of the incident X-ray beam would result in the reflection appearing as an oblique streak or an elongated elliptic spot, instead of as a round circular spot; the latter would be the observed result only when the vector cuts the sphere of reflection normally. The intensity of the streamers or elliptic spots would vary with the reciprocal phase wave-length at each point,

being greatest when this is a minimum and tending to zero when it is large. Hence, these streamers and subsidiary spots would be most prominent when the setting of the crystal is such that the Laue and quantum reflections nearly coincide. On the other hand, when the quantum reflection is far removed from the Laue reflections, all trace of them should disappear. These effects are well illustrated as the series of photographs reproduced in Figs 5 (a) to (k). A detailed discussion of them and of various other cases is given in the paper by Mr Pisharoty already cited to which the reader may be referred for further particulars. Remarkable changes in the appearances of the streamers and subsidiary spots occur when the azimuth of the setting of the crystal is altered. Some of these features are illustrated in Figs 10 (a) and (b) and 11 (a) and (b) in Plate XIX, and are in full accord with the indications of the theory.

7 Intensity of Quantum Reflection

Extremely rapid changes occur in the intensity of the quantum reflection as it approaches from the Laue spot with an alteration of the setting of the crystal. This effect is seen in the series of pictures reproduced in Figs 5 (a) to (k) and is even more pronounced than would appear from the photographs since the exposures were considerably prolonged for the first few and the last few pictures of the series. A better idea of the situation is obtained from Fig 7 which is reproduced from the article in *Current Science* for April 1940. It will be noticed that both the K_{α} and K_{β} reflections fall beyond the spot marked A and are so feeble as only just to be visible in the reproduction. The quantum reflection of K_{α} is beyond the spot marked C, while the K_{β} reflection actually coincides with the latter and therefore also with the classical monochromatic reflection. The spot marked C therefore appears very intense. The K_{α} and K_{β} quantum reflections appear respectively on the two sides of the spot marked B, the former being of great intensity. The illustration shows clearly that as the quantum reflection approaches the Laue spot, its intensity rapidly increases and ultimately becomes quite large.

It is evident from the pair of pictures appearing in Fig 8 (a) and (b) that the intensity of the quantum reflection of the monochromatic X-rays may actually exceed the intensity of the Laue reflection by the same spacings of the white radiations accompanying the characteristic X-rays of copper. That the classical and quantum reflections of the same wave-length are of comparable intensity when they are superposed is indicated by the photographs reproduced as Figs 11 (a) and (b) in Plate XIX. It will be noticed when the crystal is set so that the classical and quantum reflections coincide, the streamers emerging from the reflections on both sides are easily visible. Since these streamers are necessarily much weaker than the principal

quantum reflection, it follows that the latter should be comparable in its intensity with the classical reflection of the same wave-length which appears superposed on it. The experimental facts are thus in general accord with the conclusions arrived at from the quantum theoretical calculations set out in the preceding paper.

Experiments have also been made varying the thickness of the plate of diamond as also the width of the beam of X-rays used. These factors are found within wide limits to be without influence on the relative intensities of the classical and quantum reflections under otherwise similar conditions, thus supporting the indications of theory. On the other hand, the diffuse continuous background of scattered radiation appearing in the Laue patterns of diamond [e.g., in Figs 5 (a) to (k) and in Fig 7] is practically suppressed by using thin plates or fine X-ray beams.

8 Influence of High and Low Temperatures

The spectroscope enables us directly to observe the changes of frequency in the scattered radiations which arise when energy and momentum are exchanged between a beam of light and the crystal which it traverses. The quantum-mechanical character of such scattering is indicated by the difference of the intensities of the radiations of increased and diminished frequencies respectively. The theoretical ratio of these intensities is simply the Boltzmann factor $e^{h\nu^*/kT}$, actual measurements giving values closely agreeing with it. In the parallel X-ray problem, neither the spectroscopic observation of the change of frequency nor the comparison of the intensities of the two components ($\nu \pm \nu^*$) is at present possible. What we observe is the superposed effect of both components of frequency which, as shown in the preceding paper, is proportional to

$$\frac{e^{-h\nu^*/kT} + 1}{e^{-h\nu^*/kT} - 1} \quad (5)$$

Measurements of the variation of intensity with temperature within the range for which the formula (5) may be expected to be valid should therefore enable us to demonstrate the quantum-mechanical character of the effects and to evaluate the frequency ν^* of the vibrations responsible for them in any particular case.

As shown earlier in this paper, the 1332 vibration is the only one which can be expected to give an appreciable variation of the structure amplitude of the (111) planes in diamond. It follows from this fact and from formula (5) that the intensity of the quantum reflection by the (111) planes should be sensibly independent of temperature. This result was indicated as a consequence of theory in the *Current Science* article of April 1940. In the more

detailed paper of May 1940, experiments were described in which the diamond was heated up to 500°C without any notable enhancement of the intensity of the reflection resulting therefrom. Experiments at low temperatures were also indicated as a further test of the theory. A suitable high vacuum low-temperature X-ray camera suitable for quantitative work was then developed, and the tests made with it with the crystal cooled down to liquid-air temperatures. This was reported in a letter to *Nature*, dated the 20th September 1940 published in its issue of the 23rd November 1940. Further comparisons showed that the intensity of the reflections by the (111) planes at room and at liquid-air temperatures were practically identical. This result was communicated in a letter to *Nature* dated the 23rd November 1940 and published in its issue of the 25th January 1941.

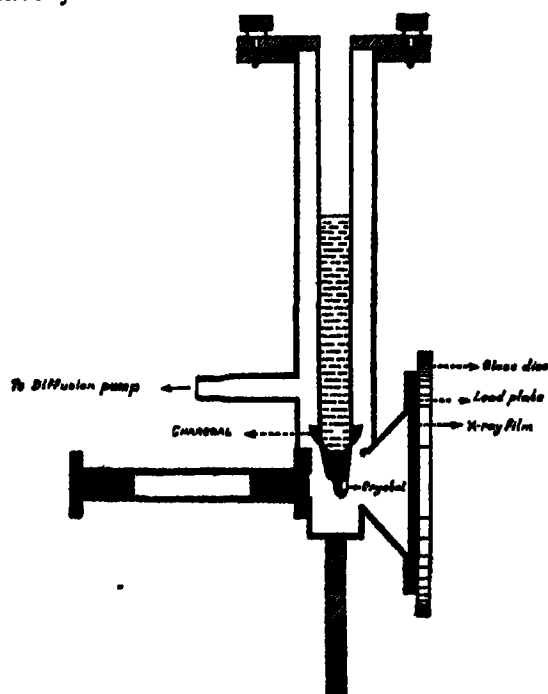


FIG 3 High-Vacuum Low-Temperature X-Ray Camera

The special X-ray camera designed and constructed for the experimental study of quantum X-ray reflections at liquid-air temperatures is illustrated in Fig 3 above. The diamond is imbedded in a copper block which forms the lowest end of the receptacle for holding the liquid air. A hole bored through the block allows passage for the X-ray beam. Both the crystal and the photographic film recording the X-ray pattern are held inside a high

vacuum, the latter being produced by an oil diffusion pump. No intensifying screen was used in these experiments. A small lead disc attached to the film served to cut off the central beam of X-rays. Photographs were taken under identical conditions with and without cooling the crystal by liquid air. Figs 12 (a) and (b) in Plate XX, reproduce two typical photographs obtained in this way, the former at liquid air and the latter at room temperature. No sensible difference is noticeable in these photographs between the intensities of the quantum reflections appearing in the vicinity of the three Laue spots. Figs 13 (a), (b) and (c) in Plate XX present a similar comparison of the intensities for the quantum reflections photographed under similar conditions at 25° and at 400° Centigrade. Here again, no difference in intensity is perceptible. The experimental results thus completely establish that the (111) reflections arise from a quantum-mechanical excitation of the infra-red vibrations of high frequency. It is important to notice that the reflections seen in Fig 12 (a) are situated in the near vicinity of the Laue reflections. Accordingly, if the effects had arisen from elastic vibrations of the lattice, these would have been of very low frequency and would therefore have been totally suppressed by the cooling of the crystal to liquid air temperature.

9 Quantum Scattering

The diffuse halo surrounding the primary beam is a very striking feature of the Laue pattern reproduced in Fig 7, the radiations here used being those of a copper target. Fig 14 in Plate XXI reproduces a similar picture taken with the X-rays from a molybdenum target and shows a noticeable contraction of the halo, but not so great as should have resulted if the halo had been due entirely to the monochromatic X-radiations present. That the halo is not due solely or even principally to the scattering of the X-rays by elastic vibrations of *thermal origin* is shown by the fact that it persists at liquid air temperatures as seen in Fig 12 (a) in Plate XX. Since the halo is recorded with the diamond inside a high-vacuum camera, it is evident that the effect cannot be due to the diffusion of the X-rays by the air. This is also otherwise clear from the fact, already mentioned, that the use of thin plates of diamond tends to suppress the intensity of the halo in comparison with those of the regular reflections. We are thus obliged to conclude that the halo is a quantum mechanical effect, the X-rays exciting the vibrations of diamond lattice having much lower frequencies than 1332 and somewhat similar characters to the vibrations of an elastic solid. The extent to which the intensity of such scattering would be diminished by lowering the temperature would be greatest for the vibrations of the lowest frequency and least for those of the highest frequency. The intensity of the halo should therefore fall off in the close

vicinity of the direct beam, and remain sensibly unaffected in directions far removed from it. The distinct sharpening of the halo at low temperatures noticed on a comparison of Figs 12 (a) and (b) is probably to be explained in this way. The outermost parts of the halo may reasonably be attributed to a diffuse scattering of the X-rays by the lattice planes of the crystal in combination with the elastic vibrations of the structure.

10 Summary

The paper presents the experimental evidence furnished by the X-ray studies with diamond which confirms the theoretical ideas and mathematical formulation contained in the two preceding papers. The nature of the vibrations of the crystal lattice of diamond is first discussed with special reference to the mode having a frequency of 1332 wave-numbers. This vibration gives a large variation of the structure amplitude of the (111) crystal planes, while other vibrations of a different character leave it unaffected. Various experimental tests show that the X-ray reflections of the second kind given by these planes are truly specular or geometric in character. Measurements of the geometric positions of the reflections over a wide range of crystal settings show a complete agreement with the theoretical formula, the phase-waves of the vibrations appearing parallel to the (100) planes of the crystal. Symmetry demands that there should be three such sets of phase-waves, and this is fully substantiated by the experimental facts. The quantum reflection moves out of the plane of incidence when the crystal plate is rotated in azimuth. The appearance of multiple spots and streamers is also explained by the theory. The intensity of the reflections is of the order of magnitude indicated by the theory and is sensibly independent of the temperature in agreement with it. The phenomenon of quantum scattering is also briefly described and discussed.

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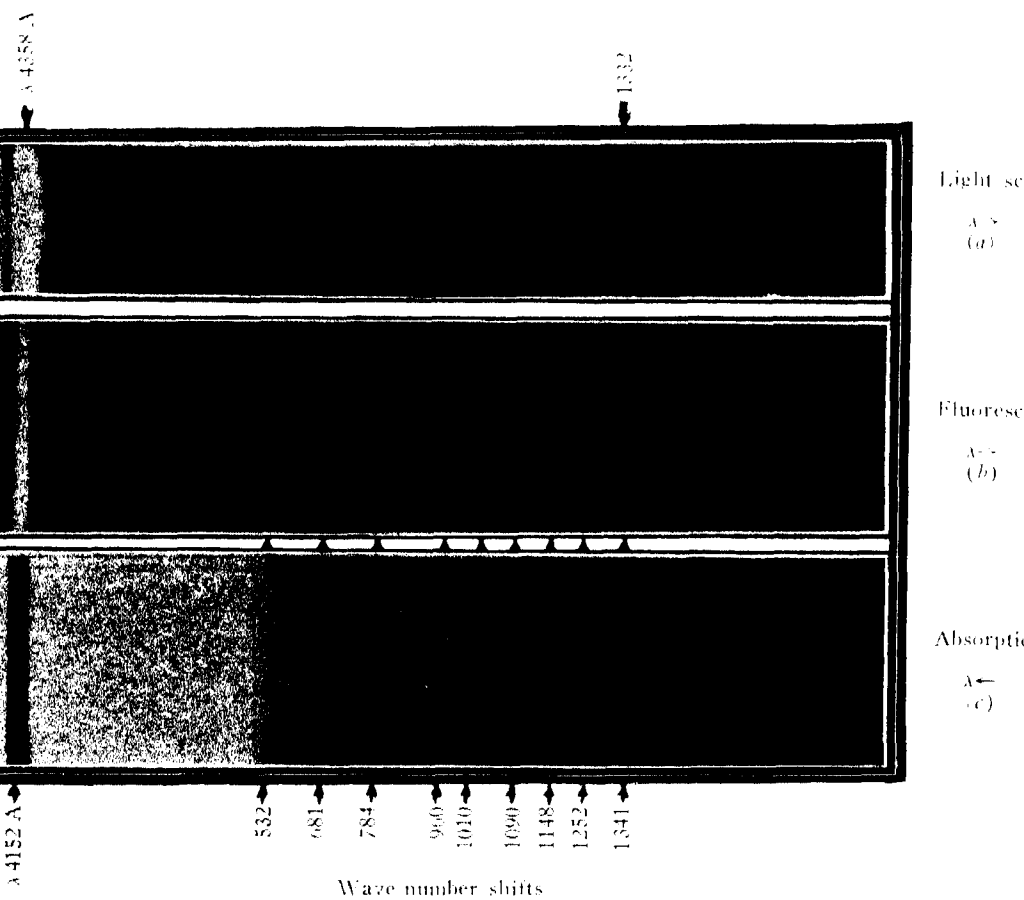


FIG. 4. Lattice spectrum of diamond appearing in (a) light scattering, (b) fluorescence, and (c) absorption.

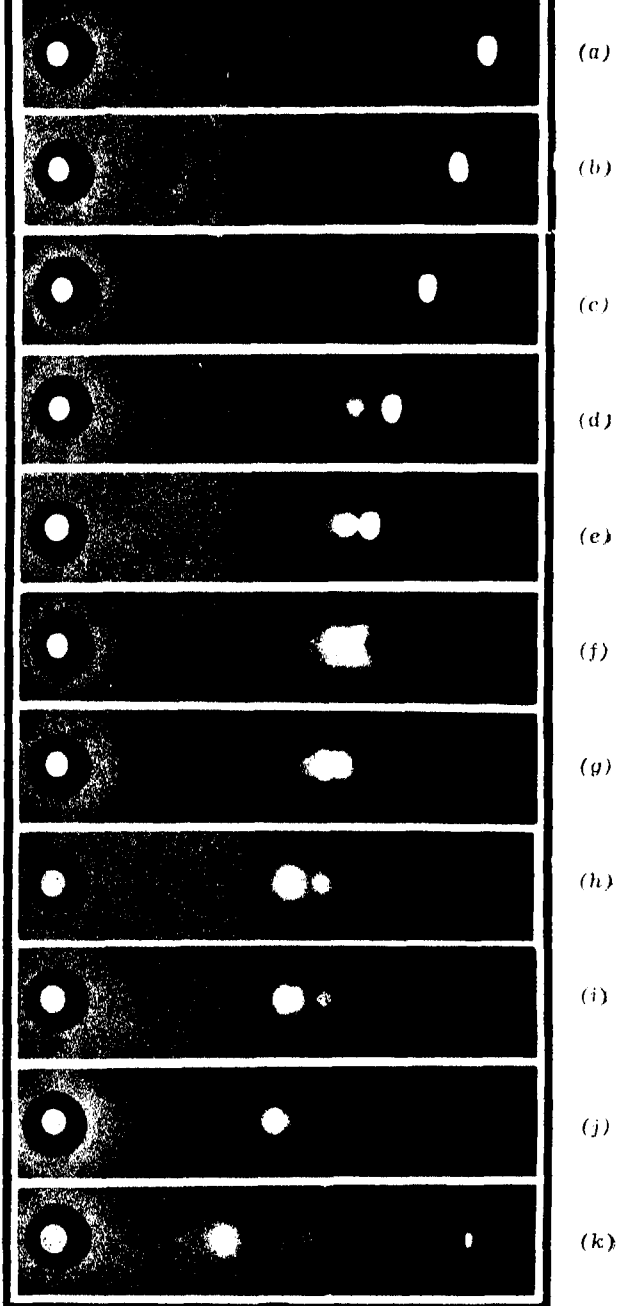


FIG. 5. Sequence of changes in (111) reflections with alteration of crystal setting.

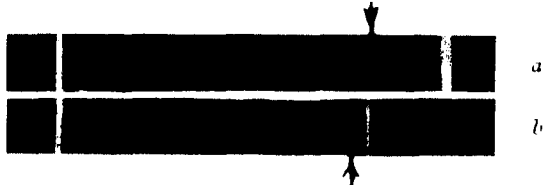


FIG. 6

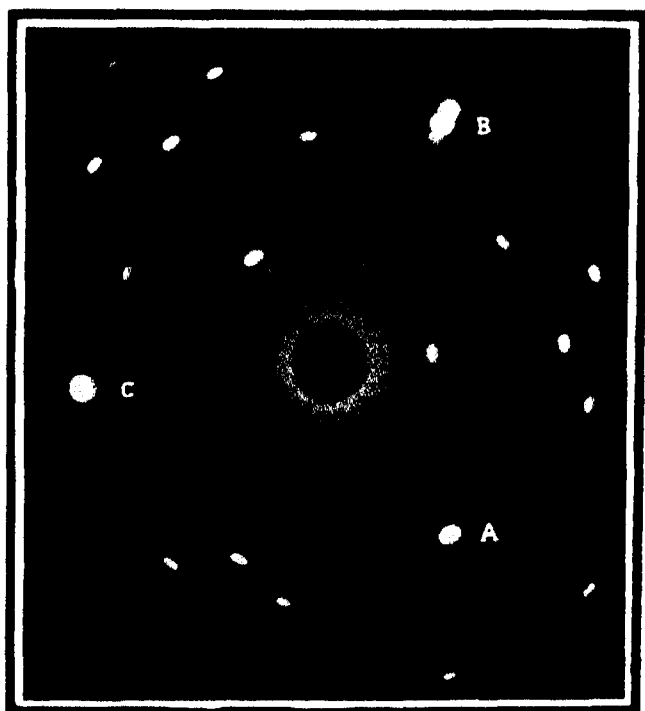


FIG. 7

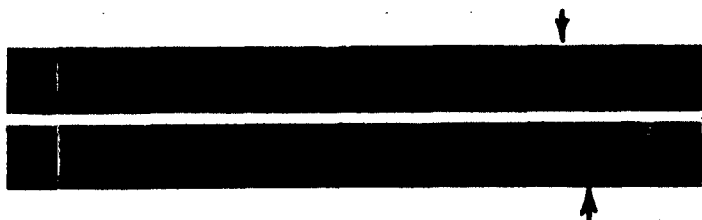
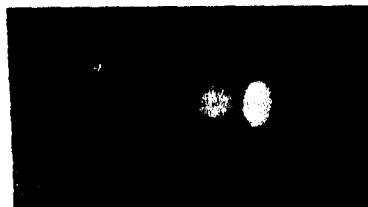
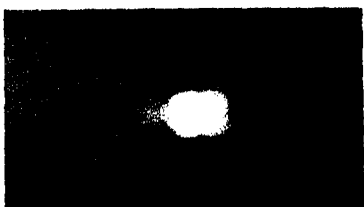


FIG. 8

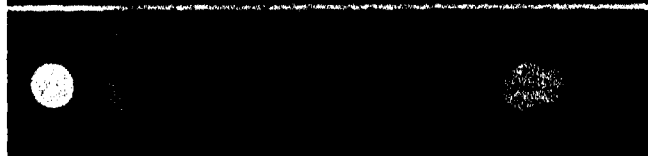


b

FIG. 9



a

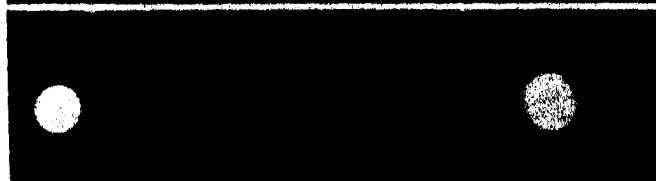


b

FIG. 10



a



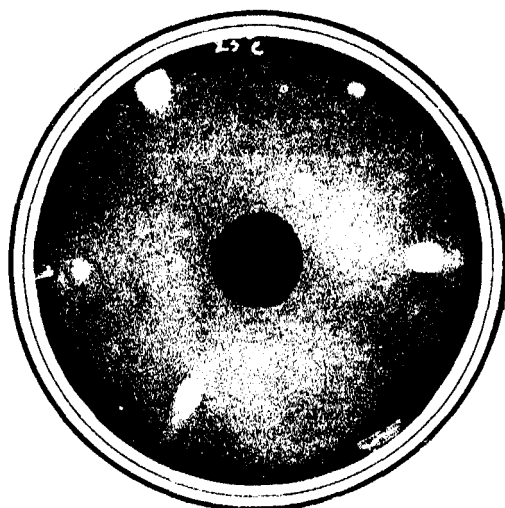
b

FIG. 11



(a)

-180 °C.



(b)

+ 25 °C

FIG. 12

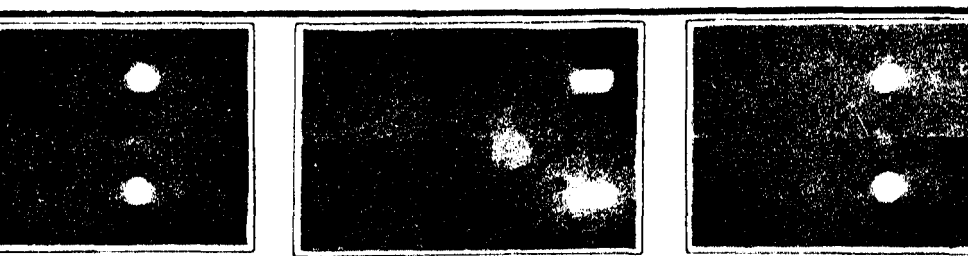


FIG. 13

FIG. 12. Quantum reflection and quantum scattering at (a), -180 °C., (b) +25 °C.

FIG. 13. Quantum reflections at +25 °C. and +400 °C.

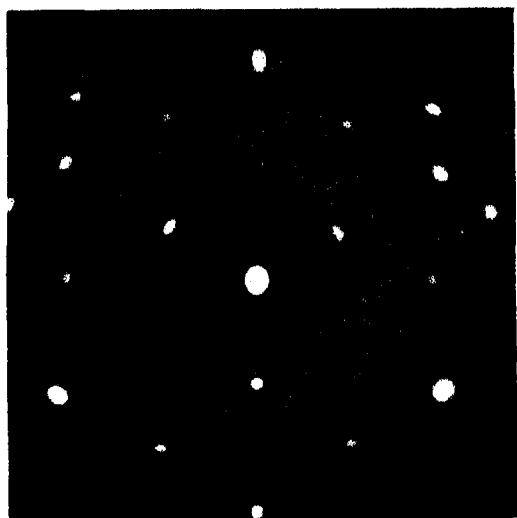


FIG. 14. Laue pattern of diamond with molybdenum radiation showing halos.

QUANTUM THEORETICAL EXPLANATION OF THE APPEARANCE OF FORBIDDEN X-RAY REFLECTIONS IN DIAMOND

BY P. RAMA PISHAROTY

(From the Department of Physics, Indian Institute of Science, Bangalore)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

a narrow pencil of monochromatic X-rays is passed through, dynamic stratifications are excited in the crystal lattice and the Raman or quantum X-ray reflections of altered frequency¹ in the particular setting of the crystal at which they are most intense co-exist with the Bragg or classical reflections by the same crystal. The present paper deals with the calculation of the structure amplitude for dynamic stratifications in the particular case of diamond on the assumption that the incident X-rays impart to each degree of freedom giving rise to an infra-red oscillation of the lattice an energy equal to $h\nu$, where ν is the frequency of the oscillation and h the Planck's constant. The simplicity of the structure of diamond and the well-known character of its active, infra-red lattice oscillations, facilitates the calculation. The planes which have zero structure amplitude for the classical reflections are shown to possess finite dynamic structure amplitudes for Raman or quantum reflections, thus accounting for the appearance of "forbidden" reflections in diamond.

2. Oscillations of the Diamond Lattice

As is well known, a crystal of diamond can be pictured as built up of two interpenetrating face-centred cubic lattices or of two interpenetrating octahedrons. On the former view the unit cell consists of eight atoms, on the latter it consists only of two atoms. Adopting the rhombohedral unit cell, Nagendra Nath² as well as Venkatarayudu³ have derived analytical expressions for the normal modes of oscillation of the diamond lattice and have shown that there is only one triply degenerate Raman active oscillation possible for the lattice. In other words, there are no Raman active oscillations for the infra-red oscillations and another three

cell of two atoms We will adopt this point of view and take the Planck oscillator in diamond to consist of two atoms and be of frequency $3\,996 \times 10^{13}$ sec⁻¹ corresponding to the shift of 1332 cm^{-1} wavenumbers exhibited by the intense Raman line

3 *The Dynamic Stratifications Associated with the (111) Reflections*

The co-ordinates of the lattice points of a unit cell of diamond, referred to rectangular axes, are known to be

$$000, \quad 0\frac{1}{2}\frac{1}{2}, \quad \frac{1}{2}0\frac{1}{2}, \quad \frac{1}{2}\frac{1}{2}0,$$

$$\text{and} \quad \frac{1}{4}\frac{1}{4}\frac{1}{4}, \quad \frac{1}{4}\frac{3}{4}\frac{3}{4}, \quad \frac{3}{4}\frac{1}{4}\frac{3}{4}, \quad \frac{3}{4}\frac{3}{4}\frac{1}{4}$$

Here the unit is 3.56 AU as obtained from the X-ray measurements. The structure amplitude F of the $(h\ k\ l)$ planes is given by the formula

$$F = \sum_p f_p e^{2\pi i (hx_p + ky_p + lz_p)}, \quad (1)$$

where f_p is the atomic scattering factor of the p th atom whose co-ordinates are x_p, y_p, z_p

When the atoms are at rest, the value of F for the (111) planes of diamond is given by

$$4f_1(1-i),$$

where we take f_1 , the atomic scattering power of the carbon atom, to be the same for all the atoms of the unit cell

We will suppose that the incident X-rays excite the infra-red vibrations of the lattice in which one lattice vibrates against the other, the direction of vibration being assumed to be normal to the (111) planes. We are justified in this as we know from the Raman effect data for diamond that its intense infra-red oscillation is triply degenerate and since the oscillations parallel to the planes themselves have no influence on their structure amplitude. We further assume, as a limiting case, that all the unit cells vibrate completely in phase and that each cell is endowed with a quantum of energy $h\nu^*$, where ν^* is equal to $3\,996 \times 10^{13}$ sec.⁻¹, the observed frequency of the lattice oscillations in diamond

The periodic displacement of the p th atom belonging to one of the lattices is given by

$$D_p = i\,dx_p + j\,dy_p + k\,dz_p \quad (2)$$

where

$$dx_p = a_p \sin(2\pi\nu^*t - \zeta) = dy_p = dz_p,$$

since the oscillation is normal to the (111) plane and all the atoms of one

lattice are in phase. The displacements of all the atoms of the other lattice are equal but opposite to those of the first.

If A be the amplitude of the oscillator taken along the $[111]$ direction, we have

$$a = \frac{A}{\sqrt{3}}$$

It is well known that the diamond lattice has three degrees of freedom corresponding to the elastic and another three corresponding to its infra-red, lattice oscillations. Hence each Planck oscillator composed of two atoms—one from each lattice—has an energy $h\nu^*$ associated with it. Therefore, if A be the amplitude of oscillation of one carbon atom and m its mass, we have

$$h\nu^* = \frac{1}{2} \Sigma mv^2 = 2 \times \frac{1}{2} m (2\pi A \nu^*)^2$$

$$\text{i.e.,} \quad A^2 = \frac{h}{4\pi^2 m \nu^*}$$

$$\text{and} \quad a^2 = \frac{h}{12\pi^2 m \nu^*}$$

Substituting the values for h , m and ν^* we obtain,

$$a = 0.0268 \times 10^{-8} \text{ cm} \quad (3)$$

We will calculate the structure amplitude of the dynamic (111) planes on the assumption that the atoms do not move appreciably in a time interval equal to the period of the X-ray vibration.

The co-ordinates of the vibrating atoms in a unit cell are

$$\left. \begin{aligned} & \frac{dx}{u}, \frac{dy}{u}, \frac{dz}{u}, \quad 0 + \frac{dx}{u}, \frac{1}{2} + \frac{dy}{u}, \frac{1}{2} + \frac{dz}{u}, \\ & \frac{1}{2} + \frac{dx}{u}, 0 + \frac{dy}{u}, \frac{1}{2} + \frac{dz}{u}, \quad \frac{1}{2} + \frac{dx}{u}, \frac{1}{2} + \frac{dy}{u}, 0 + \frac{dz}{u}, \\ \text{and} \quad & \frac{1}{4} - \frac{dx}{u}, \frac{1}{4} - \frac{dy}{u}, \frac{1}{4} - \frac{dz}{u}, \quad \frac{1}{4} - \frac{dx}{u}, \frac{3}{4} - \frac{dy}{u}, \frac{3}{4} - \frac{dz}{u}, \\ & \frac{3}{4} - \frac{dx}{u}, \frac{1}{4} - \frac{dy}{u}, \frac{3}{4} - \frac{dz}{u}, \quad \frac{3}{4} - \frac{dx}{u}, \frac{3}{4} - \frac{dy}{u}, \frac{1}{4} - \frac{dz}{u}. \end{aligned} \right\} \quad (4)$$

Here $u = 3.56 \text{ AU}$ —the side of a unit cell. Substituting these values in equation (1) and putting $h = k = l = 1$, we obtain

$$F_{111} = 4 f_1 \left\{ e^{\frac{6\pi a}{u} t \sin(2\pi \nu^* t - \xi)} - i e^{-\frac{6\pi a}{u} t \sin(2\pi \nu^* t - \xi)} \right\}$$

We have the well-known relation

$$e^{ia \sin \beta} = J_0(\alpha) + 2i J_1(\alpha) \sin \beta + 2 J_2(\alpha) \cos 2\beta \\ + 2i J_3(\alpha) \sin 3\beta + 2 J_4(\alpha) \cos 4\beta \\ + \dots$$

where $J_n(\alpha)$ represents the n th order Bessel function of α

Let us put

$$\frac{6\pi a}{u} = \alpha$$

and $(2\pi\nu^*t - \xi) = \beta$

Then we obtain that

$$F_{111} = 4f_1(1-i) [J_0(\alpha) - 2J_1(\alpha) \sin \beta + 2J_2(\alpha) \cos 2\beta \\ - 2J_3(\alpha) \sin 3\beta + 2J_4(\alpha) \cos 4\beta \\ - \dots]$$

The reflected radiation at a great distance ρ from the unit cell is given by

$$F e^{2\pi i(\nu t - \rho/\lambda)}$$

where ν is the frequency of the X-ray beam and λ its wave-length. Remembering that

$$\sin \beta = \frac{e^{i\beta} - e^{-i\beta}}{2i}, \text{ and } \cos \beta = \frac{e^{i\beta} + e^{-i\beta}}{2}$$

the expression for the secondary radiation becomes

$$4f_1(1-i) J_0(\alpha) e^{2\pi i(\nu t - \rho/\lambda)} \\ + 4f_1(1+i) J_1(\alpha) e^{2\pi i\{(\nu + \nu^*)t - \xi_1\}} \\ + 4f_1(1-i) J_2(\alpha) e^{2\pi i\{(\nu + 2\nu^*)t - \xi_2\}} \\ + \dots \quad (5)$$

This means that the secondary radiation in the direction of the classical reflection consist partly of altered frequencies. Since α is small, terms containing $J_2(\alpha)$ and higher orders may be omitted. On quantum mechanical principles the intensity of the antistokes $(\nu + \nu^*)$ will be much smaller than that of the stokes $(\nu - \nu^*)$, so that the modified radiation consists practically only of $(\nu - \nu^*)$. The ratio of the structure amplitude of this stokes' to that of the unmodified reflection is

$$\frac{J_1(\alpha)}{J_0(\alpha)} = 0.071.$$

Thus in the correct Bragg setting of the crystal, these dynamic stratifications also are capable of giving a total reflection of the X-rays with modified frequency. But due to the phenomenon of 'extinction' for the primary beam in the correct setting of the crystal, the actual percentage of the modified reflection can never exceed about 7% of the total reflected intensity. Of course this can happen only when all the Planck oscillators are in phase—a limiting case.

4 The Dynamic Stratifications Associated with the (222) Reflections

Employing the values for the co-ordinates of the atoms given by the expression (4) and substituting $h = k = l = 2$, we obtain

$$F_{222} = 4 f' \left\{ e^{i \frac{12\pi a}{u} \sin(\nu^* t - \xi)} - e^{-i \frac{12\pi a}{u} \sin(\nu^* t - \xi)} \right\},$$

where f' is the atomic scattering factor in the required direction. Let us put,

$$\frac{12\pi a}{u} = \alpha' = 2\alpha$$

and $(2\pi\nu^*t - \xi) = \beta$

so that

$$F_{222} = 8 f' [2 J_1(\alpha') \sin \beta + 2 J_3(\alpha') \sin 3\beta + \dots]$$

Hence the expression for the secondary radiation is

$$\begin{aligned} & + 8 f' J_1(\alpha') e^{2\pi i \{(\nu \pm \nu^*) t - \xi_1\}} \\ & \pm 8 f' J_3(\alpha') e^{2\pi i \{(\nu \pm 3\nu^*) t - \xi_3\}} \\ & \pm \dots \end{aligned} \tag{6}$$

We find that there can be secondary radiations of only modified frequency. In other words, if the atoms are at rest there can be no Bragg reflection at all α' being small, Bessel functions of higher orders than the first can be omitted. The intensity of the antistokes $(\nu + \nu^*)$ being negligible in comparison with $(\nu - \nu^*)$, the (222) reflection will practically consist of X-rays of frequency $(\nu - \nu^*)$ and the structure amplitude of the spacings will be

$$8 f' J_1(\alpha')$$

Its ratio to the structure amplitude of the static (111) spacings is

$$\frac{2 f' J_1(\alpha')}{(1 - i) f_1}$$

Taking the Hartee interpolation values for f' and f_1 , the above ratio works out to be nearly 0.14.

It is well known that the (222) reflection in diamond is observed^{4,5} in contradiction with the ordinary theory. It has been suggested⁴ that this may be due to the two neighbouring carbon atoms of diamond being non-centro-symmetric regarding their scattering power. This hypothesis is supported neither by the calculations of L. Pauling⁶ for the charge distribution in the carbon atom nor by the calculations of Hartee⁷ for the scattering power of the atom. The above hypothesis is further contradicted by the non-appearance of the (200) reflection.

For a specimen of diamond behaving as an ideal crystal Ehrenberg, Ewald and Mark⁵ estimate the intensity of the (222) Mo K α reflection from a rotation picture about the (110) axis to be about a third of the (400) Mo K β reflection. According to Hull the intensity ratio K α : K β for Mo is nearly 2.4. The above authors have found that the (400) reflection is about half as intense as the (111) reflection. Thus in their estimate the (222) reflection is about 0.07 times the (111) reflection.

For a perfect crystal the 'integrated reflection' is proportional to

$$F \frac{(1 + |\cos 2\theta|)}{\sin 2\theta} = F \cot \theta, \quad (\theta < 45^\circ)$$

Hence the ratio of the (222) modified reflection to the (111) unmodified reflection would be

$$0.14 \times \frac{\cot 20^\circ}{\cot 10^\circ} = 0.068$$

for the Mo K α radiation employed by those authors. This value is in excellent agreement with their observation. We may therefore reasonably infer that the (222) reflection actually observed is entirely a quantum or Raman reflection.

5 The Dynamic Stratifications Associated with the (220) Reflections

If we substitute $h = k = 2$, and $l = 0$ in equation (1) and use the co-ordinates of the atoms of the unit cell as given by the expression (4) we obtain for the structure amplitude of the dynamic (220) planes, the following expression

$$F_{220} = 8 f_2 \cos \left\{ \frac{8\pi a}{u} \sin (2\pi \nu^* t - \xi) \right\} \\ = 8 f_2 \{ J_0(a_1) + 2 J_2(a_1) \cos 2\beta + 2 J_4(a_1) \cos 4\beta + \dots \}$$

Here

$$a_1 = \frac{8\pi a}{u} \\ \beta = (2\pi \nu^* t - \xi)$$

and f_2 is the corresponding atomic structure factor

Hence the expression for the secondary radiation is

$$\begin{aligned} & 8 f_2 J_0(a_1) e^{2\pi i(\nu t - \rho/\lambda)} \\ & + 8 f_2 J_2(a_1) e^{2\pi i\{(\nu \pm 2\nu^*)t - \xi_2\}} \\ & + 8 f_2 J_4(a_1) e^{2\pi i\{(\nu \pm 4\nu^*)t - \xi_4\}} \\ & + \dots \end{aligned} \quad (7)$$

As before if we neglect the second and higher order Bessel functions of the small quantity a_1 , we find that the (220) planes cannot give rise to any modified reflection of appreciable intensity. The failure of Dr Nilakantan to record the (220) modified reflection in spite of a large number of trials is thus explicable.

6 The Dynamic Stratifications Associated with the (200) Reflections

According to the classical theory, the (200) reflection is another of the forbidden reflections in diamond. But the assumption of Planck oscillators excited by the incident X-ray quanta gives the following expression for the reflected radiation from these planes

$$\begin{aligned} & \pm 8 f_2 J_1(a_2) e^{2\pi i\{(\nu \pm \nu^*)t - \xi_1\}} \\ & \pm 8 f_2 J_3(a_2) e^{2\pi i\{(\nu \pm 3\nu^*)t - \xi_3\}} \\ & \pm \dots \end{aligned} \quad (8)$$

Here $a_2 = \frac{4\pi a}{u}$ and f_2 is the atomic scattering factor of the appropriate direction. This indicates a Raman reflection unaccompanied by any Bragg reflection. But the intensity of this modified reflection of frequency $(\nu - \nu^*)$ —the others being negligible, can only be a third of the (222) reflection. In a rotation photograph about the (110) axis the number of the co-operating planes for the (200) reflection is only two while for the (222) it is four. Ehrenberg, Ewald and Mark⁵ remark that in a rotation picture about the (110) axis the (222) reflection was just recorded while there was no indication of any (200) reflection. Their observation finds a ready explanation on this idea of lattice oscillations according to which the (200) spot has to be six times weaker than the weak (222) spot.

7. The Dynamic Stratifications Associated with the (662) Reflections

Since $h + k + l = (4n + 2)$ for this case, the (662) reflection is also 'forbidden' by the classical theory. Substituting these values of h , k and l

in (1) and using the co-ordinates given by expression (4), we obtain for the reflected radiation from the (622) planes the expression

$$\begin{aligned} & \pm 8 f_4 J_1(a_3) e^{2\pi i \{(\nu \pm \nu^*)t - \xi\}} \\ & \pm 8 f_4 J_3(a_3) e^{2\pi i \{(\nu \pm 3\nu^*)t - \xi_3\}} \\ & \pm \end{aligned} \quad (9)$$

Here

$$a_3 = \frac{28\pi a}{u}$$

and f_4 is the atomic scattering factor in the direction of this reflection

The expression shows that there is no unmodified or Bragg reflection. Neglecting the 'antistokes' and the second and higher order Bessel functions the ratio of the dynamic structure amplitude of this reflection to that of the (222) reflection is

$$\frac{f_4 J_1(a_3)}{f' J_1(a')}$$

The values of f_4 and f' of the carbon atom for the respective glancing angles of 60° and 10° , when Mo K_α radiation is employed, are found from the interpolation values obtained by the Hartree method and given in the "International Tabellen Zur Bestimmung Von Kristallstrukturen". They are 0.8 and 1.8 respectively. Substituting these values and the values of a' and a_3 , the above ratio works out to be nearly 0.9.

Since in a rotation picture the intensities of the spots on the equatorial line are proportional to

$$\frac{1 + |\cos 2\theta|}{\sin 2\theta} = \begin{cases} \cot \theta & \text{when } \theta < 45^\circ \\ \tan \theta & \text{when } \theta > 45^\circ, \end{cases}$$

the ratio of the intensity of the (662) to the (222) quantum reflection will be nearly

$$0.9 \frac{\tan 60^\circ}{\cot 20^\circ} = 0.57$$

Ehrenberg, Ewald and Mark⁵ remark that this 'forbidden' (662) reflection does appear in a rotation photograph and that it is weaker than the 'forbidden' (222) reflection, but they suggest a ratio 0.3. The discrepancy is not large when one remembers that these reflections are extremely weak and that the experimental value of the ratio of their intensities is only an estimate.

8 Other Lattice Oscillations

As mentioned in the Introduction we have here considered the rhombohedral unit cell having only one lattice oscillation which was identified as

that giving the Raman frequency of 1332 cm^{-1} . The recent work of Nayar⁸ on the luminescence and ultra-violet absorption spectra of diamond at low temperatures has revealed that the lattice spectrum of diamond contains a whole series of discrete frequencies ranging down to about 127 cm^{-1} . Amongst these, 1332 and 780 appear most prominently and are the principal members of the two important groups of frequencies. Until these modes of vibration with lower frequencies are fully investigated and can be dynamically specified, it is not possible to discuss their influence on the dynamic structure amplitudes of the various crystal planes. It may be anticipated, however, that such influence should be relatively unimportant in respect of the lattice planes for which the 1332 oscillation is active. On the other hand, it is quite possible that for those planes for which the 1332 vibration is inactive, *e.g.*, the (220) planes, the lower frequencies may influence the structure amplitudes appreciably and give rise to dynamic reflections. If this were the case, such reflections would necessarily exhibit a more marked temperature dependence of intensity than the planes which are chiefly excited by the 1332 oscillation.

I am very much indebted to Sir C. V. Raman, F.R.S., for his kind and helpful guidance in the course of this work.

9 Summary

On the Raman idea of quantum exchanges of energy and momentum between a crystal lattice and an X-ray photon traversing it, the dynamic structure amplitudes of the various crystal planes of diamond are worked out assuming that each Planck oscillator takes up one quantum of infra-red vibrational energy from the incident X-rays. It is shown that such an interaction gives rise to X-ray reflections of altered frequency in most cases. The structure amplitude of the (111) planes for this modified or Raman reflection is found to be about 7% of that of the same planes for the Bragg reflection. The (222) planes, the (200) planes, and the (662) planes, the Bragg reflections from which are 'forbidden' according to the classical theory, are found to possess finite structure amplitudes for the quantum reflections. The values of these structure amplitudes are shown to quantitatively account for the intensities of the reflections appearing from these planes as recorded by Ehrenberg, Ewald and Mark. It is therefore suggested that the so-called 'forbidden' reflections which appear in diamond are pure Raman or quantum reflections of modified frequency.

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LOW-TEMPERATURE STUDIES OF THE RAMAN X-RAY REFLECTIONS IN CRYSTALS

BY DR. C S VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

EARLY in 1940, Sir C V Raman and Dr P Nilakantan made the very significant discovery that the (111) planes of the crystal lattice in diamond give a second kind of monochromatic X-ray reflection which is as truly geometric as the usual Bragg reflection, being quite as sharply defined, but having evidently a different origin since it is observable over a wide range of settings of the crystal and obeys a different geometric law. The observed characters of this reflection indicated that it represents the X-ray analogue of the well-known Raman effect observed in the scattering of light. In other words, the X-ray photon falling upon the crystal excites the high frequency or infra-red vibrations of the crystal lattice, the latter deriving their energy from the incident X-rays. The appearance of the X-ray photon of diminished energy as a geometric reflection by the lattice planes is accounted for on the very reasonable assumption that the infra-red vibrations are excited simultaneously in all the lattice cells of the crystal with such phase relations as to give rise to a coherent effect. It follows from these considerations that if the primary X-ray frequency is ν , the reflected X-rays have a frequency $(\nu - \nu^*)$, ν^* being the frequency of the excited infra-red vibrations of the crystal.

It is well known from the Raman effect studies on the scattering of light in crystals that in general, both "Stokes" $(\nu - \nu^*)$ and "anti-Stokes" $(\nu + \nu^*)$ radiations are observed in the spectra, their absolute intensities being respectively proportional to

$$\frac{1}{1 - e^{-h\nu^*/kT}} \text{ and to } \frac{1}{e^{h\nu^*/kT} - 1}$$

and their relative intensity being accordingly $e^{h\nu^*/kT} \cdot 1$. When $h\nu^* \gg kT$, it is evident that only the component of diminished frequency would be present. On the other hand, when $h\nu^* \ll kT$, the two components tend to be of equal intensity. In the case of diamond, the observed facts indicate that the infra-red vibrations excited by the X-rays are the same as those giving the strong Raman line at 1332 cm^{-1} . Since therefore, $h\nu^*$ is much greater than kT at the ordinary temperature, it

follows that in the case of diamond we are only concerned with X-rays reflected with *diminished* frequency. It follows also, as indicated by the formulæ, that the intensity of the reflection should then be sensibly independent of temperature. This indication of theory was confirmed by Raman and Nilakantan in their earliest experiments by heating the diamond to a few hundred degrees above the room temperature, no marked increase of intensity being then observed. They also suggested as a test of the theory, the study of the effect of cooling down the diamond to liquid air temperature. This test was carried out by them a few months later, the results which were in entire accord with the theory were briefly reported at the time (1940). A more detailed description of the full technique of the investigation appears in a paper by Raman and Nilakantan elsewhere in these *Proceedings*.

It is obviously of great interest to supplement the investigations on diamond by similar researches with other crystals at low temperatures. It is evident that, in general, we would have quantum or Raman X-ray reflections of both *diminished* and *increased frequencies* superposed on each other. The observed intensity of the modified reflection should then be the sum of the two expressions quoted above. In other words, the actual intensity of the quantum reflection would be proportional to

$$\frac{e^{h\nu^*/kT} + 1}{e^{h\nu^*/kT} - 1}$$

At sufficiently low temperatures, this expression reaches the limiting value unity. On the other hand, at sufficiently high temperatures, it asymptotically tends to the value $2kT/h\nu^*$, thus becoming proportional to the absolute temperature. It is evident also that the ratio between the limiting intensity at low temperatures and the values reached at higher temperatures would depend on the frequency of the infra-red vibrations of the crystal excited by the X-rays. The higher this frequency, the more nearly would the intensity tend to remain constant throughout the whole range of temperature. On the other hand, when the frequency ν^* is low, we should have to go down to liquid air temperatures or even lower before the limiting intensity is reached.

It is evident from the foregoing remarks that the study of the quantum or Raman X-ray reflections gives us a method of investigating the infra-red spectrum of crystals from a new point of view, which should obviously prove of great importance. It should also be remarked that the study of the intensity curves of the modified reflections and their comparison with the variation to be expected theoretically from the known infra-red frequencies of the crystal, would furnish an experimental confirmation of the nature of these reflections as quantum or Raman reflections of modified frequency and

indeed enable us to determine by a thermodynamic method the actual changes of frequency occurring in such reflections. To emphasize this aspect of the matter, the present investigation has been carried out with a series of four crystals whose infra-red frequencies are in descending order of magnitude, viz., carborundum, sodium-nitrate, rock-salt and penta-erythritol.

2 Experimental Arrangements

The X-ray camera used for taking the Laue photographs at low temperatures is constructed essentially on the principles developed by Nilakantan and is illustrated in Fig 1. The crystal C is mounted in a cavity at the end of a copper rod R fixed to the bottom of the inner tube of a cylindrical metal

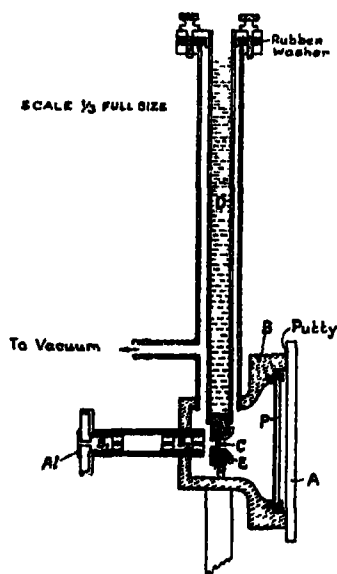


FIG 1
Low-temperature high-vacuum
X-ray camera

X-ray camera being at that temperature from the start of the exposure. In photographing the spectra, an intensifying screen is not used, as it was found that the latter becomes a serious source of error in the measurement of the intensities of spots. The X-ray generator is a demountable Coolidge tube with a Mo-anticathode and operated at 45 K V and a fairly steady milliamperage of 25 m A. Laue photographs exhibiting the Raman reflections are taken at the room temperature for the same time of exposure under identical experimental conditions. Their relative intensities are measured microphotometrically making use of a density-log intensity curve and for the same mode of development as that employed for the other

films obtained for the molybdenum radiations. In the case of rock-salt, photographs were also taken for the temperature of solid carbon dioxide and the relative intensities obtained microphotometrically were checked up by those got by an alternative method of varying the time of exposure till the intensities of the spots at the two temperatures are equal. If t_1 and t_2 are the times of exposure at the two temperatures T_1 and T_2 , the ratio of intensities $I_1/I_2 = (t_2/t_1)^n$, where n is the Schwarzschild constant which is found experimentally to be nearly unity for the X-ray film and the radiations used. Considering the limitations of the experimental method, the possible error in the values will be as high as 10%. The photographs with carborundum were also obtained at 600° T and 900° T using for the purpose an electrical heater of nichrome wire, and their intensities were compared with that obtained at the room temperature for the same setting of the crystal.

3 The Experimental Results and their Significance

Figs 2 a-h in the accompanying Plate illustrate the Laue patterns obtained with carborundum, rock-salt, sodium nitrate and penta-erythritol. It will be noticed that in every case the reflections persist at the liquid air temperature. The corresponding Laue reflections exhibit an enhanced intensity which is the greater when the diminution of intensity of the Raman reflections is most marked. This clearly indicates that the temperature dependence of the intensity of the Bragg or the Laue reflections can only be correctly explained when their relation to the Raman reflections from the same crystal planes is taken into account.

In Fig 3, the intensities of the Raman reflections at the different temperatures as compared with that given at the liquid air temperature by the

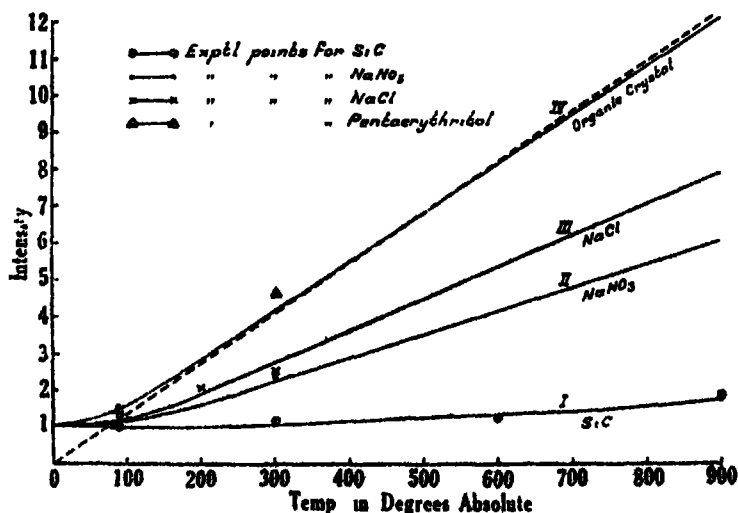


FIG. 3
Intensity of Quantum Reflections as a Function of Temperature

theory taken as the standard, are plotted along side the theoretical curves of intensities obtained in accordance with the equation given earlier and with appropriate frequencies chosen for each case (see Table I)

TABLE I

Crystal	T°	90	200	300	600	900
	$kT \times 10^{-18}$	12.3	27.4	41.1	82.2	123
Carborundum $\nu^* = 800 \text{ cm}^{-1}$	$\frac{h\nu^*}{kT}$	12.9	5.8	3.9	1.94	1.3
	Intensity (Theo.)	1	1.006	1.042	1.34	1.77
	Intensity (Exp.)	1		1.1	1.3	1.82
Rock-salt $\nu^* = 160 \text{ cm}^{-1}$	$\frac{h\nu^*}{kT}$	2.58	1.161	.774	.387	.258
	Intensity (Theo.)	1.163	1.9	2.72	5.3	7.9
	Intensity (Exp.)	1.163	1.93	2.43		
Sodium nitrate $\nu^* = 200 \text{ cm}^{-1}$	$\frac{h\nu^*}{kT}$	1.65	.74	.5	.23	.165
	Intensity (Theo.)	1.073	1.588	2.209	4.125	6.128
	Intensity (Exp.)	1.073		2.36		
Penta-crythritol $\nu^* < 100 \text{ cm}^{-1}$	$\frac{h\nu^*}{kT}$	1.65	.74	.5	.23	.165
	Intensity (Theo.)	1.48	2.82	4.08	8.14	12.1
	Intensity (Exp.)	1.48		4.59		

Carborundum—The carborundum crystal used in the investigation is a clear plate of nearly 1 mm thick and the Laue photograph shows that it belongs to the hexagonal type. The X-rays were incident nearly normal to the cleavage face. The Raman reflection appears in close proximity to the Laue reflection as a *round* spot which is fairly intense. The reflection shows only a small increase of intensity as the temperature is raised from 90° T to 900° T. This suggests that the infra-red frequency active in the Raman reflection of X-rays is relatively high. According to Schaefer and Thomas (1923), the hexagonal type of carborundum crystal shows only one strong sharp infra-red

reflection at 12μ (830 cm^{-1}) which they assume as the fundamental frequency for SiC. Accordingly, Curve 1 in Fig 3 is drawn assuming that the Raman frequency associated with the modified spot is nearly 800 cm^{-1} . It will be noticed that the experimental points all fall in the neighbourhood of this curve, indicating that the frequency change involved in the reflection is the same as the characteristic infra-red frequency.

Rock-salt—The Laue photographs of a thin plate of rock-salt are obtained for 90° , 194° and 300° T with X-rays nearly normal to the 100 plane. A lowering of the temperature is accompanied by a change of intensity of the modified reflections which approximately fits in with a frequency of 160 cm^{-1} for the active infra-red vibration as shown by Curve 3 in Fig 3. Rock-salt has only one rest-strahlen frequency at 52μ (192 cm^{-1}) and its Raman spectrum obtained by Fermi and Rasetti (1931) shows two fairly intense lines at 160 and 350 and at least two other weak diffuse maxima between 200 and 300 cm^{-1} . In a separate paper, the vibrations of the sodium chloride lattice are analysed and the X-ray active mode of vibration is indicated. The results of the present investigation show that the frequency of this vibration is in the neighbourhood of 160 cm^{-1} . In addition to a diminution of intensity, a slight sharpening of the Raman reflections is also noticeable at the liquid air temperature. This observation is of great theoretical significance, but the exact extent of sharpening can be ascertained only by using a linear slit and the reflection method for photographing it.

Sodium nitrate—The Laue patterns reproduced in Figs 2 *e* and *f* show the strong Raman reflections from the 211 plane of a crystal of sodium nitrate very near the Bragg setting in addition to other weak reflections. The relative intensities of this spot at 90° and 300° T plotted in Curve 2, Fig 3 show agreement with a vibrational frequency of nearly 200 cm^{-1} . The Raman spectrum of sodium nitrate yields two intense lattice frequencies at 98 and 185 cm^{-1} (Nisi, 1932, Nedungadi, 1938) and thus the latter is to be taken as the active vibration in the modified reflection of X-rays by the 211 plane. Raman and Nilakantan (1940) observed that if the temperature is raised to 280° C , the modified reflection of X-rays from the 210 plane gains rapidly in intensity with a corresponding fall in intensity of the Laue reflections. This observation taken in conjunction with the results obtained here suggests that the active frequency for these two planes may be different. The temperature studies of intensity of the modified reflection from various crystal planes thus affords a method of determining the mode of vibration which varies the structure amplitude of any plane to the maximum extent.

Penta-erythritol—This crystal is chosen as the representative of organic crystals of which the lattice is molecular and the units are held together by

weak van der Waals forces. The intensity of the modified reflection is considerably diminished at 90°T and is nearly one-third of that at 300°T , being thus nearly proportional to the absolute temperature. In view of this marked diminution of intensity at the liquid air temperature, it is not surprising that Lonsdale, 1940 (see Preston, *Nature*, 1941) failed to observe the same in organic crystals especially as the pattern obtained by her at the lower temperature is masked by the intense halo of liquid air. From the measurements of relative intensities made up to 90°T , it is not possible to obtain even the roughest estimate of the infra-red frequency in this case. We could however, conclude that this frequency should be less than 100 cm^{-1} as shown by Curve 4 in Fig. 3. The dotted curve by its side shows what the rate of fall would be if it were proportional to the absolute temperature. This conclusion regarding the Raman-active lattice vibration in modified X-ray reflection by organic crystals is in agreement with the experimental observation in the Raman effect that a large variety of these crystals yield discrete lattice oscillations with a frequency range of $25\text{--}120\text{ cm}^{-1}$ (Venkateswaran, 1938).

General Remarks.—The present investigation thus clearly demonstrates that the determination of the rate of change of intensity of the modified X-ray reflection with temperature provides a new method of obtaining the infra-red spectrum of crystals. The frequency of vibration could be estimated fairly accurately by measurements made at the room temperature and at liquid air temperature if it falls in the region $250\text{--}500\text{ cm}^{-1}$. For frequencies below 250 cm^{-1} , temperatures lower than 90°T will have to be employed to obtain the same degree of accuracy. The method promises to be particularly suitable for crystals for which the methods of light scattering and the infra-red absorption or reflection are not applicable.

In conclusion the author wishes to express his heartfelt thanks to Sir C. V. Raman, F.R.S., for his suggestions and keen interest in the work.

Summary

The Raman reflections of X-rays by carborundum, rock-salt, sodium nitrate and penta-erythritol are obtained at liquid air temperature with a specially designed vacuum X-ray camera and their intensities are compared with those at room temperature. For rock-salt an intermediate temperature of solid carbon dioxide and for carborundum two higher temperatures namely 600° and 900°T have also been employed. From the relative intensities of these reflections at various temperatures, the infra-red frequency active in the particular reflection is ascertained in each case making use of the following formula

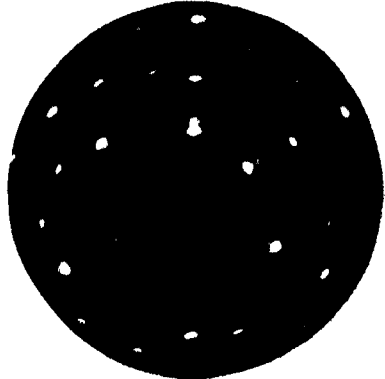
Intensity $\propto \frac{e^{h\nu_0/kT} + 1}{e^{h\nu_0/kT} - 1}$ These frequencies are about 800 cm^{-1} for carborundum, 160 cm^{-1} for rock-salt, 200 cm^{-1} for sodium nitrate and less than 100 cm^{-1} for penta-erythritol. They coincide with one or other of the low frequencies observed in the Raman effect or in the infra-red spectrum of the respective crystal. This new X-ray effect thus provides a novel method of evaluating the infra-red frequencies of crystals and is specially suitable for substances for which the methods of light scattering and infra-red spectroscopy are inapplicable.

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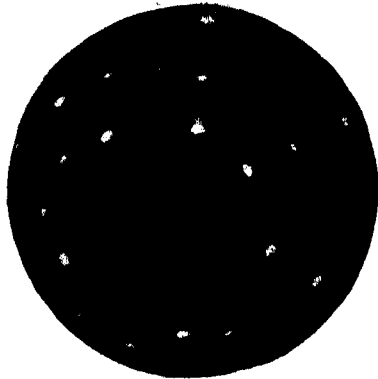
undum

(v)



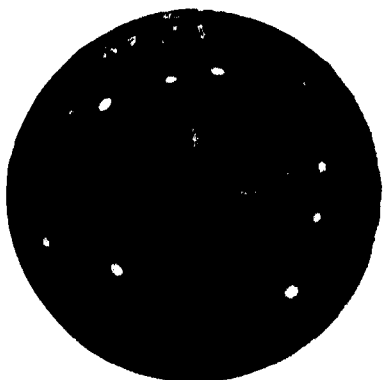
Carbon

(H)



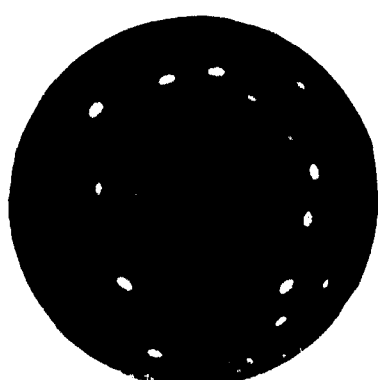
Rock-salt

(v)



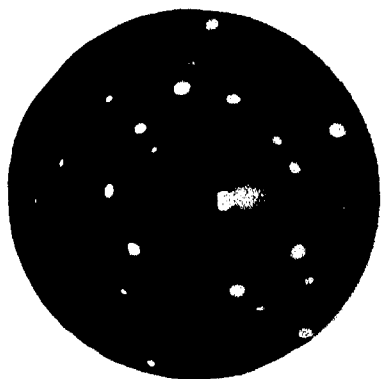
Rock

(v)



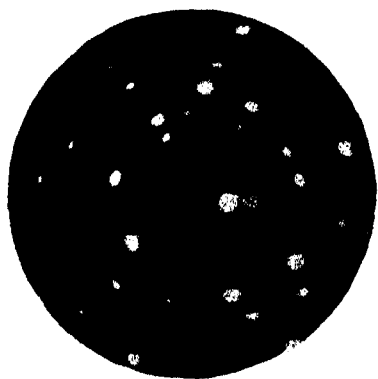
ium
rate

(v)



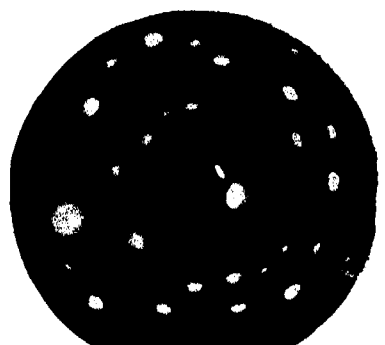
Sodium
nitrate

(v)



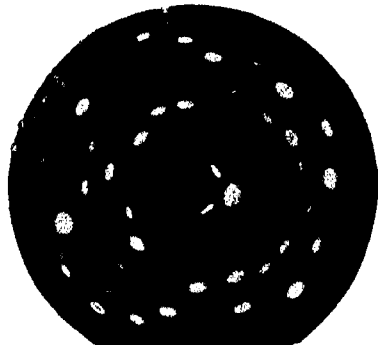
anta-
britol

(v)



Penta-
erythritol

(v)



THE QUANTUM REFLECTION AND THE QUANTUM SCATTERING OF X-RAYS IN ROCK-SALT

BY DR. C. S. VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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(Communicated by Sir C V Raman, Kt, F.R.S., N.L.)

1 Introduction

DURING the past year numerous papers have appeared concerning the origin of the diffuse spots and streaks observed by Wadlund¹ (1938) in well-exposed Laue photographs of rock-salt crystal. On the basis of their original observations on the sharply defined monochromatic X-ray reflections shown by the (111) planes of diamond over a wide range of the crystal settings, Raman and Nilakantan² (1940) put forward the view that the diffuse spots observed in rocksalt have also a similar origin, namely that they are due to a *reflection of the X-rays with a change of frequency* arising from the quantum mechanical excitation of the infra-red vibrations of the crystal lattice. About the same time Zachariasen³ (1940) put forward the view that the Faxen⁴-Waller⁵ (1923) theory of temperature-scattering of X-rays by crystals explains the phenomenon. This point of view has been supported by Preston,⁶ Lonsdale⁷ and Born⁸

In a paper in the course of publication in this *issue*, Sir C. V. Raman⁹ has theoretically examined the effect of the atomic vibrations in a crystal on the X-rays traversing it, starting from certain classical considerations originally put forward by Laue¹⁰, and has arrived at the following general conclusions. (1) The infra-red or high-frequency vibrations of a crystal lattice are quantum-mechanically excited by the incident X-ray photons, as the result of the periodic variation of the structure amplitude of particular crystal planes resulting from such vibrations, the incident monochromatic X-rays are reflected by the crystal planes with a change of frequency. *These dynamic or quantum reflections are quite distinct from the static or unmodified reflections*, except that at the Bragg setting of the crystal they coincide with the latter in direction. The direction in which the dynamic reflection appears at other settings of the crystal is determined by the inclination of the phase waves to the crystal planes. (2) The elastic or low-frequency vibrations of the crystal give rise to diffuse maxima of scattering of the kind postulated in the Faxen-Waller-Zachariasen theory.

At the Bragg settings of the crystal, the maxima are sharpest, then coinciding with the regular reflections by the lattice planes. But they fall off rapidly in intensity and become much more diffuse when the glancing angle is altered in either direction. The formulæ indicate that the direction in which the hump of scattering intensity is to be expected alters with the crystal setting roughly—but by no means exactly—in the same way as the quantum reflection by the same lattice planes. (3) In addition to this, there is a general scattering of X-rays of the Brillouin type forming a diffuse cone round the primary beam, their change of frequency being dependent on the angle of scattering. The second and the third effects due to the *elastic waves in the crystal* come under what may be called the *quantum scattering of X-rays*. The relative intensity of the quantum scattering to the quantum reflection would depend upon various factors, including especially the structure of the crystal, and the temperature of observation.

The present investigation was undertaken with the object of examining the origin of the diffuse spots observed with rock-salt by some simple experimental tests capable of deciding between the alternative theories which have been proposed.

2 *Influence of the Volume of the Irradiated Crystal*

It is well known that as a result of the primary and secondary extinctions, the number of layers of a crystal effectively taking part in the Laue or Bragg reflections is limited to an extent depending upon the degree of its crystallographic perfection. The increase of the thickness of the crystal beyond such limit results only in the loss of the intensity of reflection due to the absorption by the medium traversed. From the preliminary considerations set forth above it will be evident that a similar situation should also exist in respect of the *quantum or Raman reflections of the X-rays*. In other words, the ratio of the intensity of a Raman spot in a Laue pattern to that of any of the Laue spots due to *approximately the same X-ray wave length* should remain the same irrespective of the thickness of the crystal plate used or the narrowness of the incident beam, other things remaining the same. The size of the spots due to the quantum reflections should also increase with the area and the thickness of the crystal traversed by X-rays and with the divergence of the incident beam in much the same manner as for the Laue spots.

The situation is, however, very different for the *quantum scattering of X-rays* of either of the kinds described above. The "extinctions" restricting the number of layers in the case of a reflection do not enter into consideration and therefore, the intensity of the quantum scattering should be

proportional to the volume of the crystal irradiated except for the diminution due to absorption which arises also for the Laue or the Raman reflections. Thus, by taking a series of Laue photographs with different thickness of crystal and with varying widths of the X-ray beam traversing it, we should be in a position to decide whether we are dealing with a true reflection or a simple scattering by the crystal planes

3 Experimental Results

Figs 1, 2 and 3 in the accompanying Plate illustrate the Laue patterns obtained with molybdenum radiations incident normally to the 100 planes of rock-salt of thickness 0.5 mm and 0.25 mm respectively cleaved from the same block of a natural crystal. The diameter of the pin-hole used for the front lead slit was 1.32 mm for Figs 1 and 3 and 0.4 mm for Fig 2, which gave for the area of the crystal illumined 5.1 and 0.86 sq mm respectively. Since the intensity of the incident X-rays is diminished by the reduction of the size of the pin-hole, the time of exposure is suitably increased for the fine pin-hole in order to record the patterns with not too widely differing intensities. In comparing Figs 1 and 2, it should be noted that the thickness of the crystal and the width of the incident beam are both different, the volume of the crystal irradiated being in the ratio 12:1 as between the two cases. The ratio of the intensity of the transmitted beam to that of the incident beam, I/I_0 , for five wave-lengths is tabulated below from the known absorption data for rock-salt

Thickness of Crystal	λ in Å U	·417	·497	631	710	88
25 mm	I_1/I_0	·915	·865	·75	·665	·49
50 mm	I_2/I_0	·84	·748	·559	·45	·32
	I_1/I_2	1.09	1.09	1.32	1.48	1.53

It will be seen from the table that the effect of absorption is small up to 0.5 Å. The effect of the absorption for the softer X-rays as between the crystals of different thickness can be made out from the patterns reproduced in Figs 1 and 2. At the same time, it is clear that the relative intensity of the Laue spots and the diffuse maxima in the two photographs is practically unaltered in spite of the fact that the volume of the crystal irradiated for Fig 2 is only one-twelfth of that for Fig 1. Figs. 2 and 3 are reproductions of the Laue patterns obtained with identically the same crystal and the same setting, only the size of the pin-hole and the exposure time being varied. Although the Laue pattern in Fig. 3 is more intense than in Fig. 2, a microphotometric comparison of the intensity of the diffuse spot

due to the $\text{Mo}\cdot\text{K}_\alpha$ rays with that of the weak Laue spots in the neighbourhood shows only an increase of intensity of the order of about 10% for Fig 3 in spite of the irradiated volume on the crystal being increased nearly six-fold. It may also be noticed on comparing Fig 2 with either Fig 1 or 3 that the increased diameter of the pin-hole and the divergence of the incident beam produce very similar effects on the lateral extension of the Laue spots and the "diffuse maxima". These experimental facts conclusively prove that the intensity of the extra spots or streaks observed with rock-salt are in the main not proportional to the irradiated volume but are determined by considerations of the same kind as the intensity of the Laue or Bragg reflections. If there is any true volume scattering, it is less than one-tenth of the observed effects in its intensity.

4 The Intensity and Sharpness of the Dynamic Reflections

In the theoretical paper by Raman already referred to, it has been shown that the intensity I of the scattering at an angle 2ψ due to the elastic vibrations of the crystal is given by

$$I \propto \frac{\sin^2 \vartheta}{\sin^4 \epsilon} = \left\{ 1 + \frac{\sin^2 \theta_B}{\sin^4 \psi} - 2 \frac{\sin \theta_B}{\sin \psi} \cos \epsilon \right\}^{-1}$$

where θ_i is the angle of incidence, θ_B the Bragg angle, ϑ the inclination of the elastic wave-fronts to the crystal plane and $\epsilon = \psi - \theta_i$. Since

$$\cos \epsilon = 1 - 2 \sin^2 \epsilon/2 = 1 - 2 (\epsilon/2)^2,$$

$$I \propto \left\{ \left(1 - \frac{\sin \theta_B}{\sin \psi} \right)^2 + \frac{\sin \theta_B}{\sin \psi} (\epsilon)^2 \right\}^{-1} \quad (1)$$

This corresponds to the factor

$$\cos^2 (\theta_B - \psi) [1 + 2 \cos^2 \psi] / (\Delta \sin 2 \theta_B)^2$$

in Zachariasen's modified formula¹¹ (1941) and tends to make the intensity infinity for small values of ϵ (or Δ *). As will be seen by the curves given later in Fig 4, it also gives an asymmetrical distribution of the intensity and a shift of the maximum towards the Laue spot as in the case of the latter. But it has the added advantage that it remains valid for values of ϵ up to 20° .

In order to find whether the "diffuse maximum" in rock-salt falls off in intensity in the manner indicated by the above expression, the intensity distribution of the diffuse spots due to the 1st, 2nd and 3rd order reflections of the (200) plane of rock-salt have been determined microphotometrically from

* $\Delta = \theta_i - \theta_B$.

the same Laue photograph. A very narrow beam of X-rays emerging from a pin-hole of diameter of 0.4 mm and having a divergence of $30'$ is let fall on the 100 planes of a rock-salt crystal, 0.42 mm thick, at a glancing angle of $19^\circ 49'$. For this setting of the crystal, the maxima due to the first three orders are recorded with comparable intensities. The time of exposure is so chosen that the "maxima" are recorded with just sufficient intensity to give deflections in the microphotometer yielding a value between 0.3 and 0.6 for the log-intensities. The density-log. intensity curve for molybdenum radiations experimentally obtained was observed to be a straight line in this region and covers a range of intensity of about 1:20. Accuracy of measurement was thus ensured.

The graphs *a*, *b* and *c* in Fig. 4 are drawn with 2ψ for the abscissæ and the intensities as ordinates for the three orders. Curve 1 gives the intensity

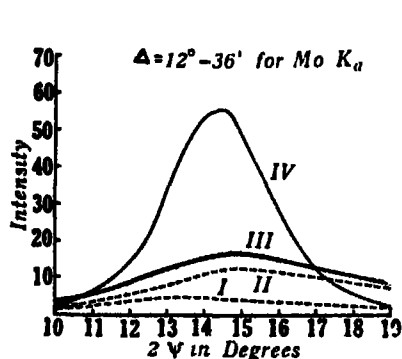


FIG 4 (a) 200 Reflections from Rock-salt

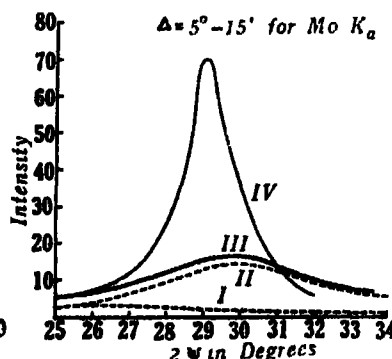


FIG 4 (b) 400 Reflections from Rock-salt

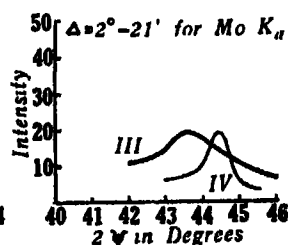


FIG 4 (c) 600 Reflections from Rock-salt

distribution due to molybdenum K_β obtained by making use of formula 1 and reduced to 40% corresponding to its relative intensity to K_α , curve 2 is that due to K_α , and curve 3 gives the sum of the two intensities. The formula takes into account the increased scattering in the higher orders of reflection. In plotting the intensities of 1st, 2nd and 3rd orders to the same scale, the calculated values were reduced in the ratio 100:19:4.87 respectively. Thus, the curves 3 in Fig. 4 *a*, *b* and *c* indicate the relative magnitudes of the intensities of the three orders and the nature of their distribution to be expected if formula I holds. Curves 4 give the observed form of distribution, the peak intensity of the 3rd order being made equal to its theoretical maximum. From a study of the curves the following conclusions may be drawn:

The half-widths obtained from the theoretical curves 3 for the 1st, 2nd and 3rd orders and measured in a direction opposite to the central spot are

$3^{\circ} \cdot 24'$, $2^{\circ} \cdot 42'$ and $1^{\circ} \cdot 40'$ The corresponding values obtained for K_{θ} only from the simplified formula of Zachariasen³ (viz., $\Delta \sin 2 \theta_B$) are $2^{\circ} 54'$, $2^{\circ} 33'$ and $1^{\circ} 40'$ respectively On the other hand, the experimental data obtained from curves 4 in Fig 4 are $1^{\circ} 50'$ for the 1st, 1° for the 2nd and $35'$ for the 3rd order It must be remarked that the finite divergence of the incident beam only tends to make the experimental values somewhat higher For regions in the close neighbourhood of the Bragg setting ($\Delta = \pm 60'$), the theoretical half-widths calculated from the simplified formula are more than 70% higher than the experimental values furnished by the careful experiments of Zachariasen and Siegel¹² (1940) The modified formula recently given by Zachariasen¹¹ (1941) also gives a higher value for the half-width* Thus we may conclude that the Raman reflections in rock-salt are much sharper than is indicated by the formula $\frac{\sin^2 \theta}{\sin^2 \epsilon}$

Secondly, it may be seen from the curves 3 in Fig 4 that if the peak intensity of the 3rd order is taken as unity, that of the 1st and 2nd orders should be 0.9 and 0.85 respectively On the contrary, the observed peak intensity of the 1st order is 2.9 times and that of the second order 3.7 times these theoretical values, showing thereby that the fall of intensity of the spot with increasing values of ϵ is much less rapid than is represented by the above formula. These experimental facts clearly demonstrate that neither as regards the variation of half-width of the spot nor of its intensity with crystal orientation, do the so-called "diffuse maxima" in the Laue pattern of rock-salt obey the laws appropriate to the scattering of X-rays by the elastic vibrations of the thermal origin in the crystal

In conclusion the author expresses his sincere gratitude to Sir C. V. Raman, Kt., F.R.S., N.L., for his stimulating interest in the work

5. Summary

The 'diffuse maxima' in the Laue patterns of rock-salt are obtained for two different crystal thickness and two different sizes of the pin-holes in the lead slit, the ratio of the volumes of the crystal irradiated by X-rays in the two cases being nearly 1.6 and 1.12 A comparison of their intensity with the weak Laue spots in the same pattern does not show any appreciable change due to the increase of the volume of the crystal. It is also noticed that the increase of the diameter of the pin-hole and the divergence of the X-ray beam has the same effect on the shape and dimensions of the Laue

* The half-widths given by curves I and II in Fig. 4 in the paper by Zachariasen (1941) are for a pin-hole and give therefore only the lower limit for the linear slit used by Zachariasen and Siegel.

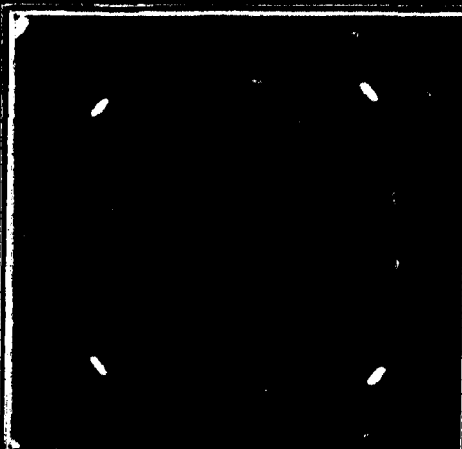


FIG. 1

Crystal thickness 0.5

Area illumined 5.1 sq

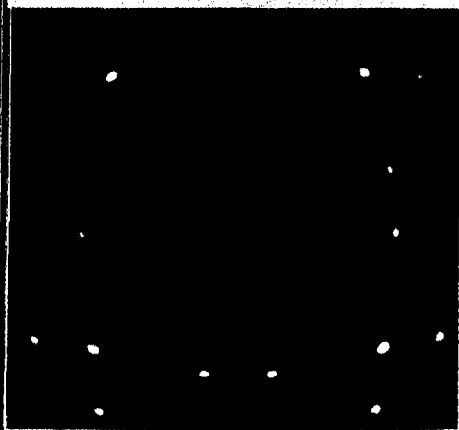


FIG. 2

Crystal thickness 0.2

Area illumined 0.8 sq

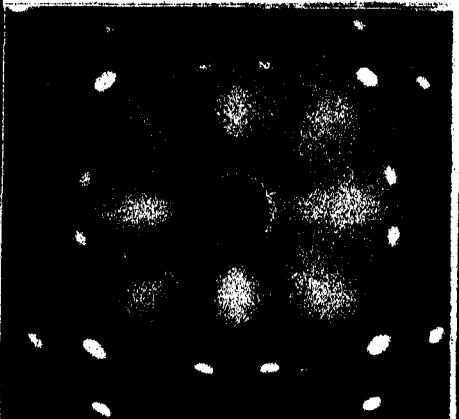


FIG. 3

Crystal thickness 0.25

Area illumined 5.1 sq

spots and of the diffuse maxima. A microphotometric study of the intensity distribution of the 1st, 2nd and 3rd order spots due to the (200) planes of rock-salt reveals that they are much sharper and that the fall of intensity for increased angles of reflection is much less rapid than is to be expected if they were due to the scattering of X-rays by the thermally excited elastic waves in the crystal. It is therefore concluded that these diffuse maxima in rock-salt are due mainly to the *quantum or Raman reflections* of the X-rays due to the excitation by the X-ray quanta of the monochromatic or infra-red vibrations of the crystal lattice.

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THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: I. NAPHTHALENE

BY DR C S VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

ONE of the most remarkable and significant facts in crystal physics brought to light by recent investigations is the appearance of monochromatic vibrations of very low frequency as a very general feature in the lattice spectra of crystalline solids. The Raman spectra of practically all crystals, both of the inorganic and the organic class, and of the most varied type, *e g*, elements, ionic and molecular lattices, exhibit lines with low frequency shifts. These lines (of which there may be several) appear with the solid, often with notable intensity and sharpness, but disappear or else are replaced by a continuous spectrum when the substance melts or passes into solution. The literature of the subject has been reviewed by the author¹ in a paper in the Raman Jubilee Volume (1938) where studies of the phenomenon in several organic crystals are also described. The origin of these low frequency lines is now well understood to be due to the oscillations of the atoms, ions, or molecules in the lattice with respect to one another, such oscillation being either hindered translations or hindered rotations according to circumstances. Such vibrations being of low frequency, they are strongly excited by thermal agitation and appear with both diminished and increased frequency in the spectra. Simple considerations indicate that a large proportion of the thermal energy of the solid, especially in organic crystals where there are several molecules in the unit cell, must be taken up by such low frequency monochromatic vibrations. It is also evident that such vibrations would powerfully influence the structure amplitudes of the lattice planes and hence must play a notable part in determining the effects resulting from the passage of X-rays through the crystal.

Considering the experimental facts stated above and also the theoretical ideas developed by Sir C V Raman in a paper appearing earlier in these

Proceedings, it follows that the passage of X-rays through an organic crystal should result in the excitation of the specific modes of vibration having these low frequencies and hence also in a dynamic reflection of the X-rays by the lattice planes whose structure amplitudes are varied by such vibrations. Further, the character of these reflections, *viz.*, their intensity, geometric direction, sharpness and their temperature variations should exhibit the closest correlation with the geometry, frequency and amplitude of these modes of vibration. As the frequencies of these modes are usually low (30 to 100 cm^{-1} in spectroscopic units), their intensity should show a strong temperature dependence, diminishing rapidly with a fall of temperature, but reaching a limiting value at the lowest temperatures. A study of the typical case of pentaerythritol from this point of view has already appeared in an earlier paper by the present writer in these *Proceedings*. In order to illustrate other aspects of the subject, a detailed study has been made of three cases, *viz.*, naphthalene, benzophenone and urotropin in which we have a detailed knowledge both of the crystal structure and also of the low frequency infrared vibrations from the studies of their Raman spectra

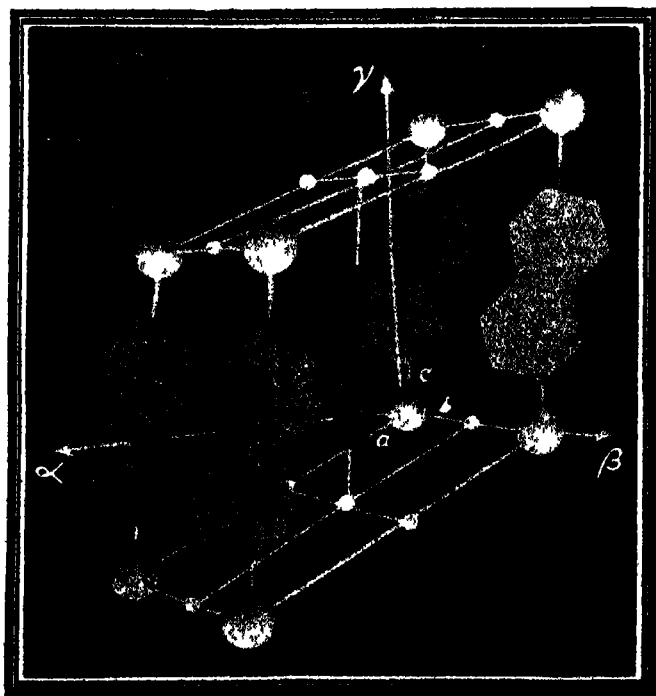


FIG. 7. Crystal Model of Naphthalene

2 Crystal Structure and Lattice Spectrum of Naphthalene

Naphthalene $C_{10}H_8$ belongs to the monoclinic prismatic class in the space group C_{2h}^2 . The unit cell has the dimensions $a = 8.29$, $b = 5.95$ and $c = 8.68$ Å and $\beta = 122^\circ 42'$ (Bragg,² 1921, Banerji,³ 1930, and Robertson,⁴ 1933) and contains 2 molecules of $C_{10}H_8$. The molecule consists of two fused benzene rings lying in a plane. The orientation of the molecules in the crystal is illustrated in Fig. 7* taken from a paper recently published by Nedungadi. The long axis of the molecule makes angles of $\phi = 115^\circ 3'$, $\psi = 102^\circ 6'$ and $\omega = 28^\circ 7'$ and the short axis $\phi' = 71^\circ 2'$, $\psi' = 28^\circ 8'$, $\omega' = 69^\circ 1'$ respectively with a , b and c' axes (c' is perpendicular to a and b) of the crystal. The orientation of the second molecule in the centre of unit cell is given by the glide plane reflection of the corner molecule in the 010 plane, the glide plane being parallel to the 'a' axis. The above crystal structure of naphthalene is in agreement with the magnetic and optical anisotropies observed in the crystal.

The molecule of naphthalene belongs to the symmetry class D_{2h} (Kohlrusch,⁵ 1935, Bonino,⁶ 1936; Saxena,⁷ 1938) and has 48 normal modes of internal vibration, 24 of which are active in the Raman effect and 20 in the infra-red. In the crystal these internal vibrations of the two molecules in the unit cell presumably remain the same, as is shown by the identity of the Raman spectrum of the substance in the liquid and in the crystalline state (Nedungadi,⁸ 1941). The total of twelve degrees of rotational and translational freedom of the two molecules together, give rise to the lattice oscillations and the Debye elastic waves in the crystal, *nine* of them being assigned to the former and *three* to the latter. Thus it is clear that the elastic vibrations would contribute only a relatively small part of the thermal energy of the crystal at the room temperature. Since the crystal possesses a low order of symmetry, the nine lattice oscillations are most probably all non-degenerate. In the Raman spectrum of naphthalene crystal, four lines have been observed (Gross and Vuks,⁹ 1935, 1936; Venkateswaran,¹ 1938; and Nedungadi,⁸ 1941) which have to be definitely attributed to the lattice vibrations. Fig. 8 in the accompanying Plate reproduces the spectrum of a single crystal of naphthalene photographed by Nedungadi. As the frequencies are low, they are thermally excited at the room temperature as is shown by the almost equal intensities for the Stokes and anti-Stokes Raman lines in the spectrum.

3 Dynamic X-Ray Reflections in Naphthalene

The X-ray analogue of the Raman effect in naphthalene was studied by Bhagavantam and Bhimasenachar¹⁰ (1941). They observed the dynamic

* In Fig. 7, a , β and γ are the axes of the optical polarisability ellipsoid

X-ray reflections by 001, 002 and $20\bar{1}$ planes of naphthalene, but these were recorded only when the crystal orientations were nearly the same as those required for the static reflections. For other orientations and other planes they were unable to observe the spots presumably because the source of X-rays used by them was not sufficiently strong. The more powerful equipment available at this Institute has made a thorough investigation possible. A thin plate of naphthalene crystal, prepared from a solution of a mixture of alcohol and water, is mounted on a goniometer with the 001 (cleavage) plane lying in a vertical plane. The source of X-rays was a demountable self-rectifying filament X-ray tube with copper anti-cathode and run at 25 mA and 45 kilo-volts. As the crystal sublimates rapidly, a series of twelve Laue photographs were taken in succession with an exposure time of half an hour in each case. Figs 1 and 2 in the accompanying Plate are the patterns obtained with the incident beam making a glancing angle of $6^{\circ} 45'$ and $11^{\circ} 42'$ with the 001 plane, being thus very near the Bragg angles for the first order ($6^{\circ} 5'$) and for the second order ($12^{\circ} 7'$) reflections from that plane for the copper K_{α} radiations. It may be noticed that the static reflections are recorded with great intensity in both the photographs. But there is only a faint indication of the dynamic reflection of the first order in either case. In Fig 1, the second order dynamic reflection is recorded weakly as a diffuse spot in the same line as the central spot and the 001 Laue spot. At the same time the *weak* Laue spot in a direction making an angle of nearly 120° with the 001 Bragg reflection, is accompanied by a *strong* dynamic reflection. In Fig 2, the latter is very close to the Laue spot showing that the crystal is very near the Bragg setting for the corresponding crystal plane. From the distance of this spot from the centre and the intensity of the Bragg reflection and the setting of the crystal, the plane is identified as $0\bar{1}1$ plane. Figs 3-6 are taken with the crystal rotated both about the vertical and horizontal axes. It may be observed that several crystal planes give rise to Raman reflections. For the normal incidence on the 001 plane of naphthalene, the X-rays are making a glancing angle of $4^{\circ} 15'$ with the $20\bar{1}$ plane, which varies only slightly as the crystal is rotated about a vertical axis. Thus in Figs 3 and 4, for which the 001 plane lies in a vertical plane, the angles of incidence of the Laue spot due to $20\bar{1}$ plane, which may be observed vertically above the central spot, are $4^{\circ} 59'$ and $4^{\circ} 44'$. The crystal planes corresponding to the other dynamic reflections could be identified from their position on the plate, the angle they make with $20\bar{1}$ reflection and with each other and the known orientation of the crystal.

Table I gives the indices of these planes, the glancing angles* of incidence θ , and the angle of reflection $(\theta + \phi)$, the spacing d calculated from the relation, $2d \sin \frac{(\theta + \phi)}{2} = n\lambda$ for the Raman reflection, the estimated intensity

TABLE I

No	Indices of Plane	Ref to Fig	θ	$\frac{1}{2}(\theta + \phi)$ for K_{α}	Lattice Spacing in A U		Intensity (Dynamic)	Intensity (Static)	
					Experimental	Calculated		Bragg	Robertson F'
1	001	1	6° 45'				w	v st	27.5
		2	11° 42'	5° 55'	7.476	7.3	v w	"	"
2	002	1	6° 45'	12° 9'	3.65	3.65	"		15.5
		2	11° 42'				w		"
3	011	1	12° 50'	9° 33'	4.63	4.66	v st	0	6
		2	11° 0'	9° 33'	"	"	"		"
4	110	3	6° 54'	9° 40'	4.52	4.58	st	st	37
5	111	4	11° 12'	9° 27'	4.68	4.63	med	med	
6	120	3	17° 42'	16° 30'	2.7	2.77	w		12.5
7	201	3	4° 59'	10° 46'	4.115	4.12	med	st	40
		4	4° 44'	10° 33'	4.2	"	"	"	"
		5	8° 32'	"	"	"	"	"	"
		6	14° 51'	"	"	"	"	"	"
8	211	3	13° 56'	12° 52'	3.45	3.39	"	"	
		4	7° 22'				v w		
		5	7° 56'	12° 48'	3.47	3.39	med	st	
9	202	5	6° 11'	12° 28'	3.56	3.72	"		21.5
		6	11° 18'	"	"	"	"		"
10	200	6	12° 52'	β 11° 18'	3.546	3.46	"	st	40
11	211	3	5° 56'	β 10° 47'	3.645		"		
12	222	4	16° 30'	17° 52'	2.5	2.32	"		14
13	222	5	16° 11'	17° 42'	2.53		w		

Note —v st =very strong, st =strong, med =medium intensity, w =weak and v w =very weak, F' =structure factor

of the latter and the intensities of the corresponding static reflections given by Sir William Bragg (1921) and Robertson (1933). It is clear from the data given in the above table that the intensity of the dynamic reflections from the

* The plate distance for Figs 1 and 2 is 5.2 cm. and for Figs 3-6 is 5.7 cm.

crystal planes is by no means proportional to the intensity of the corresponding Bragg reflection. The most intense modified spot is given by the $0\bar{1}1$ plane which has a low structure factor. The planes 110 , $20\bar{1}$, $21\bar{1}$ and 200 which have the highest structure factors also give rise to modified spots with medium intensity. On the other hand, in spite of the fact that the 001 plane, according to Sir William Bragg, gives the strongest reflection and has a large structure factor, the first and second order dynamic reflections by it appear only extremely weakly. The experimental results thus clearly demonstrate that the intensity of the dynamic reflections are determined by considerations very different from those controlling the intensity of the static reflections by the same planes.

4 *Significance of the Experimental Results*

The basic idea in the quantum theory of X-ray reflection in crystals is that the frequency of the incident radiation is modulated by the monochromatic infra-red vibrations of the crystal. In an earlier paper appearing in this issue it has been shown that the frequencies lying in the region of $30\text{--}100\text{ cm}^{-1}$ are alone effective in the modified X-ray reflections by organic crystals. Therefore for the purpose of the present discussion, we may ignore the internal vibrations of the naphthalene molecule. Since the plane of the molecules in the crystal is nearly *normal to the 001 plane*, five rotations and two translations out of the nine possible lattice vibrations involve movements *parallel to the 001 plane*. Therefore, these vibrations do not affect the structure amplitude of the latter. As the displacements of the molecules due to the remaining two lattice vibrations normal to 001 planes are also relatively small, the dynamic reflections of the X-rays from this plane resulting from those lattice vibrations should be expected to be relatively weak. The opposite situation prevails for the planes $0\bar{1}1$, 110 , $20\bar{2}$ and $21\bar{1}$. The plane of the molecule is nearly parallel to them and all the lattice vibrations make their maximum contribution to the variation of the structure amplitude. Thus, even when the static structure factor is low as for $0\bar{1}1$, the Raman reflection will be very strong. The crystal planes 200 , $20\bar{1}$, 120 and $11\bar{1}$ lie between these two extremes with respect to the lattice vibrations and the dynamic reflections from them will, therefore, be of medium intensity as compared with the corresponding Bragg reflection. The experimental facts observed in the present investigation are in good agreement with these conclusions.

The observations include a wide range of crystal planes making angles between 55° and 125° with the cleavage plane. It is obvious that the almost total disappearance of the reflection from the 001 plane which gives one of the strongest Bragg reflections and the great intensity of the reflection from

the $0\bar{1}1$ plane which has a very low structure factor cannot be accounted for on the basis of the Faxén-Waller theory (Zachariasen, 1940) that the observed spots are the maxima due to the diffuse scattering of X-rays by the elastic waves in the crystal

In conclusion I express my sincere gratitude to Sir C V Raman, F R S, N L, for his suggestions and interest in the work

5 Summary

The Raman X-ray reflections from 001 , $0\bar{1}1$, 110 , $11\bar{1}$, $20\bar{1}$, 200 , $20\bar{2}$, 120 , $21\bar{1}$, $22\bar{2}$ and $2\bar{2}2$ planes of a naphthalene crystal are obtained. It is observed that the first and second orders of the dynamic reflections from 001 (cleavage) plane are extremely weak, in spite of the fact that its static structure factor is high. On the other hand, these reflections from $0\bar{1}1$ plane which has a very low structure factor, are very strong. The 110 , $20\bar{1}$, $21\bar{1}$ and 200 planes which give the strongest Bragg reflections also yield the Raman spots with medium intensity. These experimental facts are readily explained in relation to the known crystal structure and the lattice vibrations of naphthalene, if we assume the basic idea in the quantum theory of X-ray reflection in crystals put forward by Raman and Nilakantan that the frequency of the incident radiation is modulated by the monochromatic infra-red vibrations of the crystal lattice. A study of the relative intensities of the dynamic reflections from the different crystal planes clearly demonstrates that the character of these reflections is determined by the geometry and amplitude of the lattice vibrations.

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FIG.

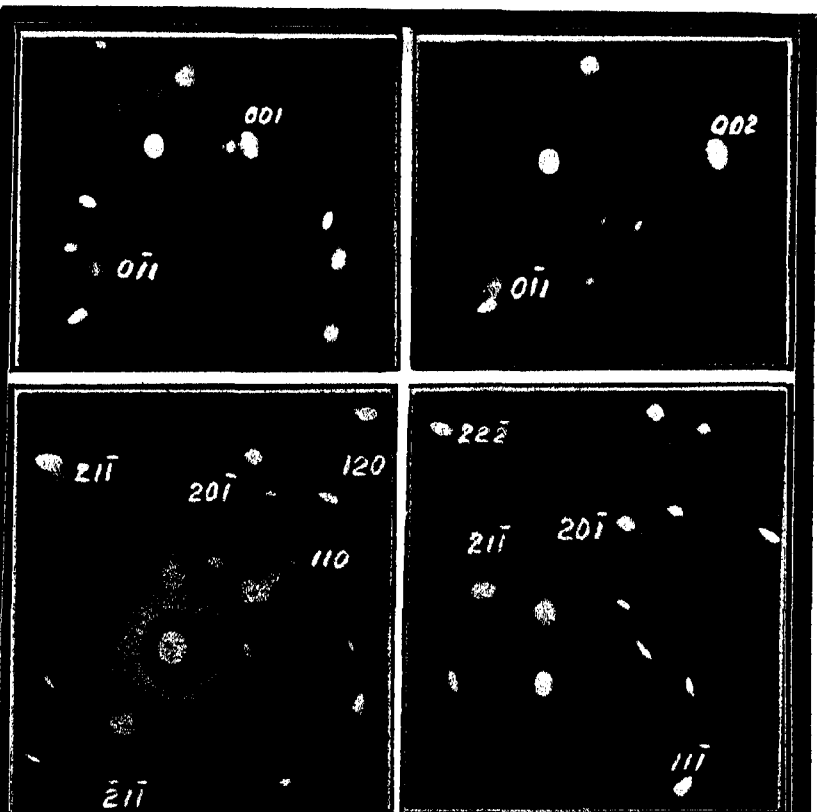


FIG.

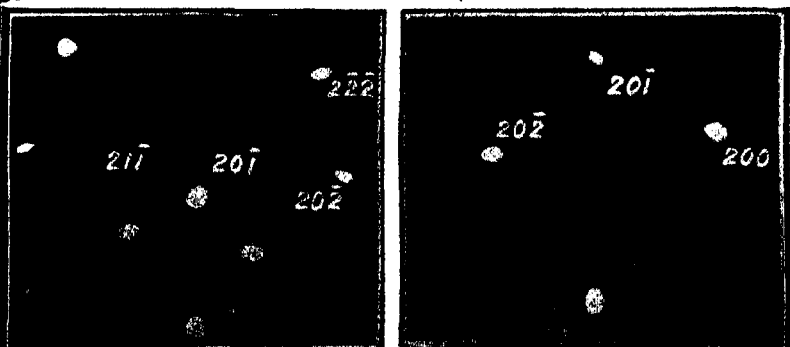


FIG.

THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: II. BENZOPHENONE

BY DR. C. S. VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

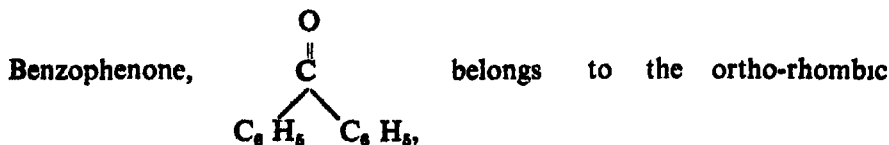
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1 Introduction

IN the first paper of this series, it was shown that the dynamic or Raman X-ray reflections from the 001 plane of naphthalene almost completely disappear as a necessary consequence of the fact that the plane of oscillating molecules in the lattice is nearly normal to this crystal plane. An exactly opposite effect is noticed in benzophenone crystal in which the intensity of the dynamic reflection is abnormally high for the 001 plane. As in the case of naphthalene, the intensity of such reflections as compared with the static ones, is also observed to depend on the orientations of the crystal and the molecular planes in the lattice

2 Crystal Structure and Lattice Spectrum of Benzophenone



bisphenoidal class (Groth¹), having a space group $D_2^4 P2_1 2_1 2_1$ (Banerji and Haque², 1938). The dimensions of the unit cell are $a = 10.3$, $b = 12.11$ and $c = 8.04$ A.U. There are four molecules in the unit cell. The X-ray analysis of the crystal structure is incomplete, but Banerji and Haque² have observed that most of the important crystal planes yield very strong Bragg reflections, the absent reflections being from *hoo*, *oko* and *ool* where h , k and l are odd. Krishnan, Guha and Banerji³ (1933) have given the magnetic susceptibilities along the a , b and c axes as $\psi_a = -88 \times 10^{-6}$, $\psi_b = -88.6 \times 10^{-6}$ and $\psi_c = -149.3 \times 10^{-6}$ e.m.u. The refractive indices along the three directions γ , β and α (parallel to the crystal axes a , b and c respectively) are $\gamma = 1.67$, $\beta = 1.65$ and $\alpha = 1.52$ (Nedungadi⁴, 1941). It has been concluded from the above data of magnetic and optical anisotropies that the two benzene rings linked through the carbonyl group $C=O$ are inclined to each other at an angle of $22^\circ 35'$, the plane bisecting the two

benzene rings being *normal* to the 'c' axis. The line of intersection of the two benzene planes is inclined to the 'a' and 'b' axes, the angle made with the 'b' axis being $22^{\circ}35'$. Thus the biplanes of the molecule are nearly *parallel* to the 001 plane of the crystal, which is just the opposite of the condition prevailing in naphthalene.

The benzophenone molecule $(C_6H_5)_2CO$ has sixty-three possible internal vibrations. Twenty-seven of these have been observed in the Raman spectrum of the melt, of which twelve are depolarised (Nedungadi, 1941). In the crystal, in addition to these intra-molecular vibrations for each of the four molecules in the unit cell, which do not show any significant changes from the liquid, there are *twenty-four* degrees of rotational and translational freedom for the molecules, of which *twenty-one* contribute to lattice vibrations and *three* only to the Debye elastic spectrum. In the Raman spectrum of the crystal, it has been observed that the intense "wing" of the liquid on either side of the Rayleigh line is replaced by three discrete lines* at 67, 102 and 122 cm^{-1} (Venkateswaran, 1938, Gupta, 1938; and Nedungadi, 1941). It has been shown by the present author that the line at 122 has to be assigned to the deformational oscillation of the two benzene rings against each other and the other two to the lattice vibrations. Nedungadi (1941) has studied the variations of intensity of the *Raman lines* in a single crystal of benzophenone with different crystal orientations and concluded that his observations are in good agreement with the above conclusions regarding the orientation of molecules in the unit lattice.

3 The Dynamic Reflection of X-rays by Benzophenone

X-rays from a copper target are employed. A small crystal of benzo-phenone measuring approximately $2\text{ mm} \times 2\text{ mm} \times 1\text{ mm}$ is mounted with the 110 plane lying in a vertical plane. Three sets of Laue patterns are obtained, the first set with X-rays nearly grazing the 110 plane, the crystal being rotated about a vertical axis; the second set with X-rays incident nearly normally on the 110 plane, the crystal being rotated about a vertical axis and the third set of pictures being taken in the same way as the second set but with the crystal rotated about a horizontal axis. Figs. 2 and 3 in the accompanying Plate are the Laue patterns obtained for the first set with X-rays making glancing angles of $4^{\circ}19'$ and $8^{\circ}24'$ respectively with the 110 plane. Figs 4 and 5 are the patterns for the second set, the X-rays making glancing angles of nearly 8° and 2° with 110 plane. Figs 6 to 9 are the photographs obtained for the third set,

* See Fig 1 in the accompanying Plate

TABLE I

No	Ref to Fig	Indices of Plane	2θ	$\theta_1 + \phi$ for $K\alpha$	Lattice Spacing in A U		Angle* made with 001	Intensity (Dynamic)	Intensity (Static) (Banerji)
					Exp	Theo			
1	6	002	12° 10'	21° 12'	4 18	4 02	0°	v v str	v str
	7	"	19° 54'	22° 4'	4 02	"	"	"	"
	8	"	29° 38'	21° 12'	4 18	"	"	"	"
2	2	012	24° 59'	22° 29'	3 94	3 82	+166°	med	
	6	"	21° 12'	23° 13'	3 82	"	+162°	str	
	5	012	20° 20'	22° 29'	3 94	"	- 15°	"	
3	1	102	19° 28'	22° 29'	3 94	3 75	-159°	med	
	4	"	21° 12'	22° 54'	3 87	"	-160°	"	
4	4	121	24° 9'	20° 47'	4 26	4 38	- 160°	med	
5	1	022	31° 28'	27° 18'	3 26	3 35	+ 34	med	
	4	"	28° 22'	26° 59'	3 3	"	"	"	
	1	022	22° 54'	26° 58'	"	"	+144°	str	
	2	"	27° 21'	26° 34'	3 35	"	+146°	"	
6	4	"	20° 47'	26° 58'	3 3	"	"	"	
	1	202	22° 3'	23° 19'	3 4	3 2	- 38°	str	v str
	3	"	19° 28'	26° 59'	3 3	"	"	"	"
	7	"	22° 4'	27° 44'	3 21	"	- 36°	med	"
7	4	122	24° 9'	28° 8'	3 2	3 19	-41°	w	
	3	111	18° 9'	15° 53'	5 56	5 62	45°	w	v str
8	5	"	19° 28'	15° 25'	5 73	"	"	med	"
	"	111	"	"	"	"	135°	"	"
9	6	132	29° 38'	32° 11'	2 76	2 75	- 48°	med	
	7	"	34° 15'	32° 53'	2 72	"	- 47°	"	
10	6	021	9° 47'	14° 57'	5 91	5 86	+130°	med	
11	2	201	17° 42'	20° 47'	4 3	4 34	60°	med	
	3	"	22° 4'	19° 54'	4 45	"	- 58°	"	
	6	"	15° 53'	19° 54'	"	"	- 69°	"	
12	5	131	24° 58'	26° 10'	3 4	3 41	- 65°	v w	
13	1	110	8° 38'	11° 13'	7 87	7 85	90°	med	v str
14	2	210	16° 48'	18° 9'	4 87	4 74	90°	w	
	3	210	16° 47'	"	"	"	"	"	
15	5	220	28° 8'	22° 4'	4 017	3 93	90°	v w	v str
	6	"	26° 34'	22° 29'	3 94	"	"	"	"
16	5	130	27° 44'	23° 44'	3 74	3 76	- 90°	v w	v str
17	5	140	28° 8'	30° 45'	2 89	2 9	90°	v w	v str

* + sign means clockwise and - sign, anti-clockwise

Note —v v str = very very strong, v str = very strong, str. = strong, med = medium, w = weak, v w = very weak

the glancing angles made with 001 plane being nearly 0° , 6° , 10° and 15° respectively. The prominent streak appearing in all the patterns is due to the 001 plane and serves as a guide for the identification of different crystal planes giving rise to Raman reflections. In Table I the visual estimates of intensities of the dynamic and static reflections are given along with the indices of the corresponding planes, the angle they make with the 001 plane at the Bragg setting, and their lattice spacings obtained from the position of the Raman spot by making use of the formula $2d \sin \frac{(\theta_s + \phi)}{2} = \lambda$, and the spacing calculated from a knowledge of the crystal structure. Only the Raman spots seen in the neighbourhood of the Bragg setting are included in the table, though many of them are present in the other photographs as well.

The outstanding result of the present investigation is the enormous intensity of the dynamic reflections from the 002 plane of the crystal. The intensity of the Bragg reflection from this plane is only as much as that of several other crystal planes, but on a rough estimate its dynamic reflection is at least ten times more intense than the most prominent spot from any other plane. The data given in Table I and the photographs reproduced in Figs 2 to 9 further show that the following planes making an angle between $0-40^\circ$ on either side of 001 and 00 $\bar{1}$ planes also yield Raman spots with fair intensity: 01 $\bar{2}$, 10 $\bar{2}$, 12 $\bar{1}$, 022, 02 $\bar{2}$ and 202. On the other hand, the Raman reflections from the planes making an angle of nearly 90° with it, namely 110, 2 $\bar{2}$ 0, 210, 2 $\bar{1}$ 0, 130, 1 $\bar{4}$ 0 and 131, are comparatively weak. Banerji and Haque have given estimates of intensities of the Bragg reflections for only a few of the planes given in the above table. A comparison of the relative intensities of the static and dynamic reflections for these planes, however, reveals that there is no direct relationship between the intensities of both cases.

4 Significance of Experimental Results

From the above observations of the intensities of the Raman reflections from several crystal planes of benzophenone, it is clear that the intensity is a maximum when the plane is nearly parallel to the plane of the molecule and a minimum when it is nearly perpendicular to it. The results are thus analogous to those obtained for naphthalene in the earlier paper and are readily explained on the same basis as the latter. Since the unit cell of benzophenone contains four molecules, there are twenty-one possible modes of lattice oscillations; but as the exact position and orientation of the molecules in the lattice are not known, it is not possible to analyse these

vibrations and ascertain the degeneracies involved. However, it is obvious from the known disposition of the molecules in the lattice that most of the lattice vibrations will contribute components normal to the 001 plane, thus causing a large variation of the structure amplitude of the plane. On the other hand the motions of the molecules during these vibrations being nearly parallel to the family of planes situated normal to 001 plane, their contribution to the dynamic structure factor of these planes will be a minimum. The results of the present investigation are thus in good accord with the proposed crystal structure of benzophenone.

As only three out of twenty-four degrees of rotational and translational freedom of the molecule in the unit lattice contribute to the Debye spectrum, the fraction of the total thermal energy carried by the elastic waves in the crystal is almost negligible. The diffuse scattering of X-rays by these waves should therefore be relatively very feeble, and cannot account for the great intensity of the new spots observed in the Laue photographs. Secondly, it is also evident from the habit of the crystal and its physical properties that benzophenone is much more nearly isotropic than naphthalene. This would lead us to expect the intensity of the diffuse scattering of the X-rays by the elastic vibrations by the different crystal planes to have intensities nearly in proportion to the ordinary X-ray reflections by those planes. The striking disparity actually observed in the relative intensities of the dynamic and static reflections from different planes recorded in the present investigation therefore precludes the possibility of any connection between the observed phenomena and the theory of diffuse X-ray scattering by the elastic waves in the crystal.

In conclusion the author wishes to express his respectful homage to Sir C. V. Raman, F.R.S., for his sustained interest in the work.

5 Summary

The dynamic reflections of X-rays from several crystal planes of benzophenone are recorded. The striking observation made in the investigation is that the intensity of the reflection from 002 plane is enormously great. Other planes on either side of the latter making angles of 0° – 40° , also give rise to Raman spots of fair intensity. On the other hand such reflections from planes making an angle of nearly 90° with the 001 plane are comparatively weak, in spite of the fact that they give very intense Bragg reflections. These experimental results are thus in striking contrast with those obtained for naphthalene in which the dynamic reflection from the 001 plane is almost completely absent. These facts are readily

explained on the basis of the theory due to Raman and Nilakantan that they arise from the vibrations of the crystal lattice. The difference in the behaviour of these reflections for naphthalene and benzophenone is due to the fact that while in the former the plane of the molecule is normal to the 001 plane, in the latter it is parallel to the 001 plane.

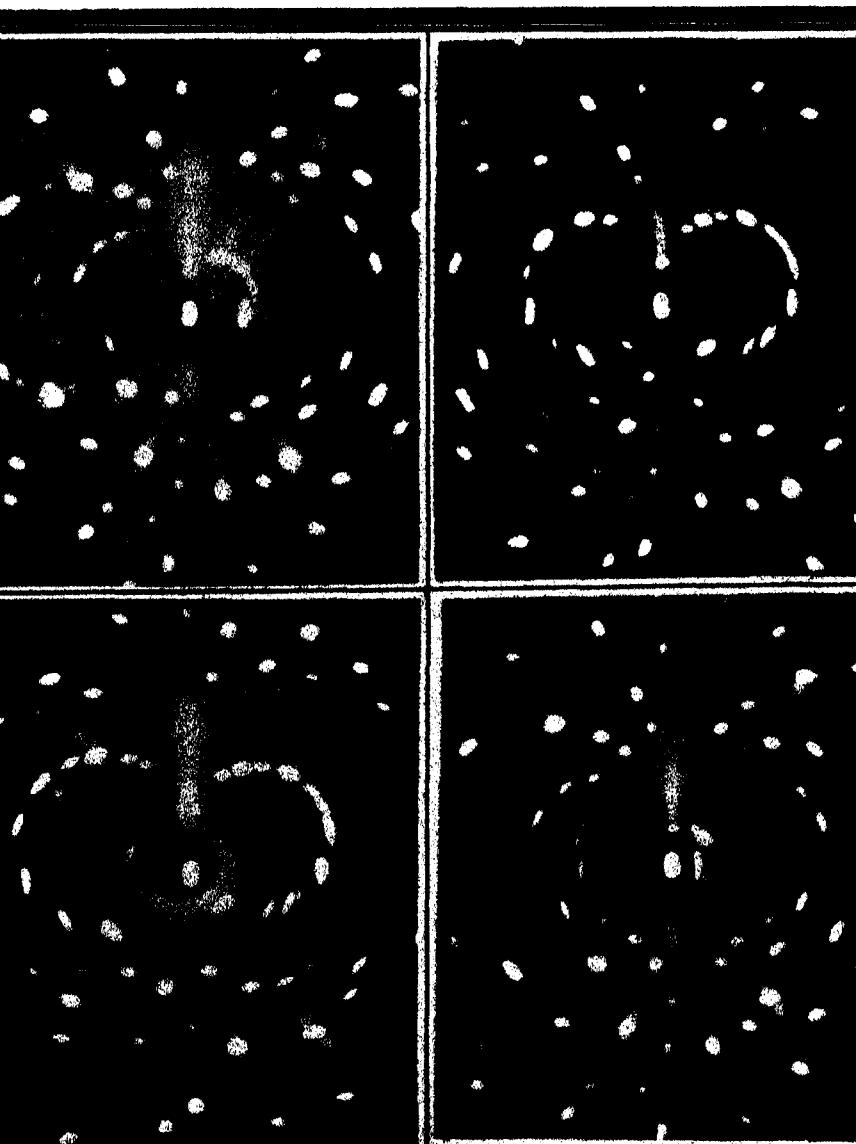
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Fig. 2

Fig. 3



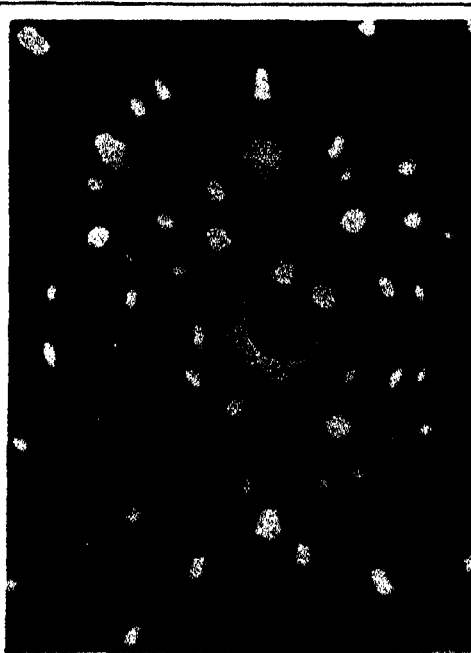
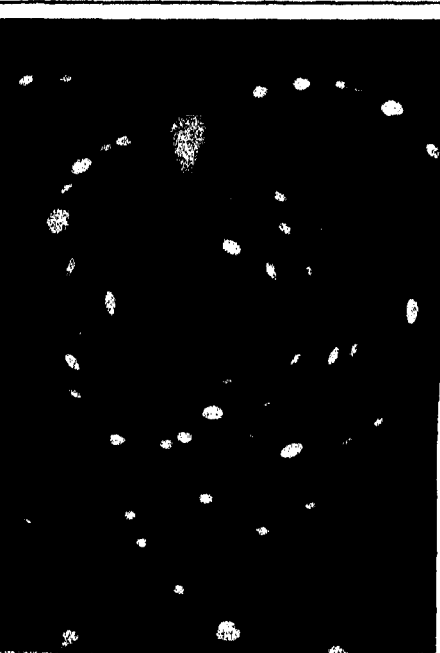
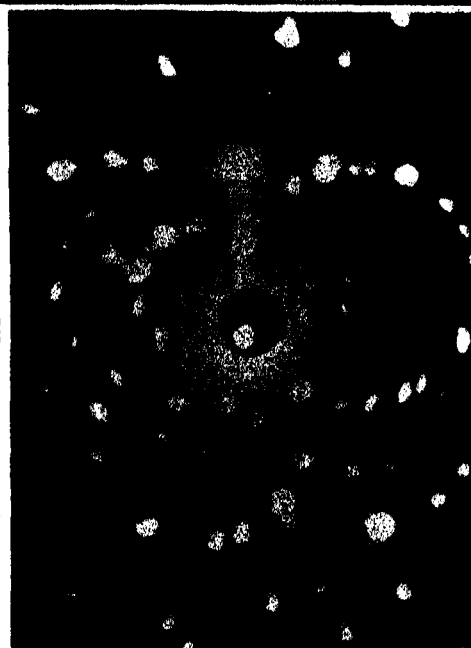
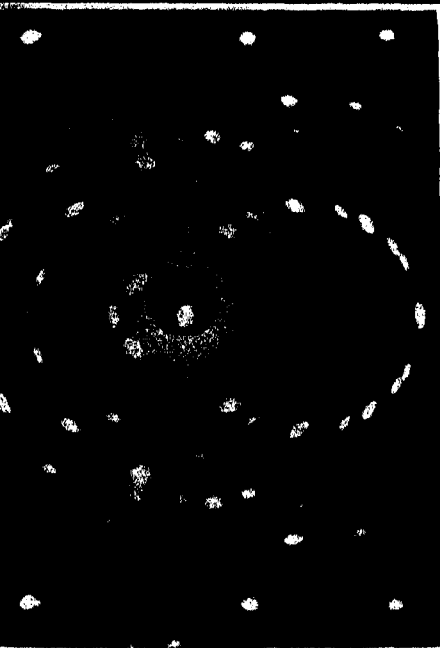


FIG. 8

FIG. 9

THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: III. HEXAMETHYL-TETRAMINE

BY DR. C. S. VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.I.)

1. Introduction

THE two earlier papers of this series dealt with crystals of aromatic compounds, viz., naphthalene and benzophenone. The molecules of these crystals being highly anisotropic in shape, the effect of their translatory and rotational oscillations would be very different on crystal planes respectively parallel and perpendicular to the plane of the aromatic rings. As a result, a striking disparity in the relative intensities of the dynamic and static reflections from the different planes was observed. For the sake of comparison it is of great interest to consider the phenomena observed with hexamethyl-tetramine which is one of the few well-studied organic substances crystallising in the cubic system. On the basis of the ideas already indicated we should expect to find in this case a closer parallelism between the intensities of the Raman and Bragg reflections by the planes of the crystal. This conclusion is strikingly supported by the experimental results.

2. Crystal Structure and Lattice Spectrum of Hexamethyl-tetramine

The crystal structure of hexamethyl-tetramine—urotropin—has been investigated by Gonell and Mark (1923), and Dickinson and Raymond (1923), and with especial thoroughness by Wyckoff and Corey (1934). The unit cell is a body-centred cube having an edge-length of $a = 7.02$ A.U. and contains two molecules of $C_6H_{12}N_4$. The only planes giving first order reflections are those having two odd and one even indices.

The molecule $C_6H_{12}N_4$ possesses a symmetry T_d . Due to the high order of symmetry, many of the molecular vibrations are degenerate. There are ten modes of vibrations characteristic of the ring, of which eight are Raman active and four are infra-red active. Kohlrausch and co-workers (1938) have observed all these eight lines below 1500 cm^{-1} , besides the C-H vibrations. In the crystal the two molecules of the unit cell which give in general, all the internal frequencies observed in aqueous solutions, possess

in addition twelve degrees of rotational and translatory freedom which yield the lattice and the acoustic spectra. Since the crystal has an O_h symmetry and the molecule is isotropic, it is easily seen that these will yield only one inter-molecular vibration (or hindered translation) along the diagonal of the unit cube, which is triply degenerate, and two hindered rotations which are also triply degenerate. A group-theoretical analysis of the crystal vibrations shows that the translatory vibration comes under the symmetry class F_{2u}^* which is inactive in the Raman and the infra-red. One of the rotatory vibrations belongs to the class F_{1g} and is inactive in both Raman and infra-red. The other appears in the class F_{2g} and is active only in the Raman. A preliminary investigation made to record the lattice spectrum of the crystal yielded only a weak picture which indicated a faint line below 100 cm^{-1} . A detailed investigation of this region with single crystals is now in progress.

3 *The Dynamic Reflections of X-rays by Hexamethyl-tetramine*

A tiny crystal of urotropin prepared from a solution of a mixture of water and alcohol was used in the investigation. The experimental arrangement was the same as that described in the previous communications. The X-rays were first made incident normally to the 110 plane of the crystal, which is one of its natural faces. A series of twenty-eight Laue photographs were taken with the crystal rotated about the vertical cube-edge from 0° to 45° . Figs 1 to 8 in the accompanying Plate reproduce some of the typical photographs obtained. Fig 1 gives the pattern when the X-rays are exactly normal to 110. The two strong dynamic reflections from 110 and $1\bar{1}0$ and four weak reflections from 011 and $0\bar{1}1$ and 101 and $10\bar{1}$ forming an irregular hexagonal pattern may be clearly observed. Besides, the four Raman spots due to (211) planes are also recorded in the neighbourhood of the corresponding Laue spots. Figs 2 to 8 are for the positions of the crystal for which the goniometer readings are nearly 2° , 7° , 26° , 30° , 33° , 37° $30'$ and 45° respectively. The only crystal planes which give Bragg reflections within the range included in the present investigation are (110), (200), (211), (220) and (222). All these reflections may be easily identified from the patterns illustrated in the Plate. Measurements of the positions of the spots were, however, made from all the twenty-eight photographs taken and the representative data are given later in Tables II to IV.

* The notations are those used by Placzek in *Handbuch der Radiology*, Vol 2, page 297.

4 Experimental Results and their Discussion

1 *Relative intensities of the dynamic and static reflections*—Table I gives the estimated intensities of the Raman spots of the different planes and the intensities of the Bragg reflections given by Wyckoff and Corey (W and C) and Gonell and Mark (G and M)

TABLE I

Indices of planes	Intensity (Dynamic)	INTENSITY (STATIC)	
		W & C	G & M
110	v str	1281	v str
200	med	447	m str
211	str		str
220	v w	300	w
222	str		str

It will be seen that the intensities of the dynamic and the static reflections are proportionate for the five planes which represent four totally different directions in the crystal. Of the three lattice vibrations of the crystal, the two hindered rotations do not change the structure amplitude of the principal planes. Hence the only vibration which is active in the Raman X-ray reflections is the hindered translation which is triply degenerate. This affects the structure amplitudes of various planes to a similar extent †

2 *The sharpness and orientation of the Raman spots*—One of the significant observations made on the Raman spots from the (100), (110) and (211) planes of the crystal is that they are fairly sharp and well-defined if not too far removed from the Laue reflections. This is in striking contrast to the 'diffuse' spots that are usually recorded in crystals, *e.g.*, rock-salt or benzophenone or highly complicated structures like sorbic acid (Lonsdale, *etc.*, 1941). This is no doubt connected with the fact that there is only one lattice oscillation which modulates the incident X-rays and the dynamic reflections in each case arise from a single set of phase-waves. When there are more than one lattice vibration involved, the observed Raman spot is the result of the superposition of a series of reflections from several phase-waves which make different angles with each other. This is presumably one of the reasons why most of the organic and inorganic crystals yield only diffuse spots at angles even slightly different from the Bragg setting.

† Theoretical calculation shows that the (100) and (111) reflections which do not appear in the Bragg are weakly active in the Raman X-Ray effect.

It may further be noticed from the illustrations that for oblique incidence, the orientation of the Raman spots is different from the corresponding Laue spots. Pisharoty (1941) has shown in a recent paper that while the Laue spots are elliptical, the Raman spots are round in shape as a consequence of the fact that the total deviation of the ray from the incident beam remains nearly constant for small changes in the angle of incidence. When the cross-section of the incident X-ray beam is not circular, but elongated as in the present investigation, the Raman spots should for the same reason, have the same shape as the direct spot and be parallel to its length. This is what is observed in the case of spots from (110) and (211) planes. It may also be observed from Figs 2 and 6 that as the static reflection by (211) planes recedes away from the dynamic reflection, the latter deviates slightly from the line joining the central and the Laue spots. This indicates that the phase-wave responsible for the (211) dynamic reflection is not normal but inclined to the plane containing the incident beam and the normal to the crystal plane.

3 *The geometry of the dynamic reflections*—Tables II to IV give the lattice spacing d calculated for the different planes at different crystal orientations by making use of the Raman-Nath formula (1940),

$$2d \sin \frac{\theta + \phi}{2} \sin \left(\theta + \frac{\phi - \theta}{2} \right) = \lambda \sin \theta,$$

where θ is the glancing angle of incidence and $(\theta + \phi)$, the angle made by the spot-maximum with the central ray and ϕ , the inclination of the phase-waves to the crystal planes. It may be seen that in the case of (200) and (110) planes, the spacing d remains nearly constant and equal to the theoretical value over a wide range of angles, if we take $\theta = 90^\circ$. When the

TABLE II

(200) Reflections Phase Wave-angle $\theta = 90^\circ$ Crystal Spacing $= 3.501 \text{ \AA}$

No	X-ray Wave-length	2θ	$\theta + \phi$	$\phi - \theta$	Calculated Spacing in \AA
1	CuK $_{\alpha}$	15° 52'	25° 12'	9° 20'	3.455
2	"	19° 27'	"	5° 45'	3.448
3	"	23° 48'	"	1° 24'	3.443
4	"	30° 53'	25° 26'	— 5° 27'	3.415
5	"	34° 50'	"	— 9° 24'	3.426
6	"	36° 42'	"	—11° 16'	3.429

TABLE III

(110) Reflections Phase-wave Angle $\vartheta = 90^\circ$ Crystal Spacing = 4 964 Å

No	X-ray Wave-length	2θ	$\theta + \phi$	$\phi - \theta$	Calculated Spacing in Å
1	CuK α and CuK β	0°	16° 40'	16° 40'	5 102
2	"	7° 49'	16° 54'	9° 5'	4 995
3	CuK α	11° 6'	17° 25'	6° 19'	5 089
4	"	12° 42'	17° 40'	4° 58'	5 023
5	"	13° 30'	17° 55'	4° 25'	4 940
6	"	16° 54'	17° 40'	0° 46'	5 007
7	"	20° 26'	17° 55'	- 2° 31'	4 940
8	"	24° 17'	17° 40'	- 6° 37'	5 014
9	"	28° 20'	17° 50'	- 10° 30'	4 942
10	"	29° 12'	17° 55'	- 11° 17'	4 96

TABLE IV

(211) Reflections X-Ray Wave-length = 1 537 Å Crystal Spacing = 2·865 Å

No	2θ	$\theta + \phi$	$\phi - \theta$	CALCULATED SPACING IN Å	
				$\vartheta - 90^\circ$	$\vartheta - 65^\circ 54'$
1	26° 34'	30° 53'	4° 19'	2 889	2 84
2	29° 12'	31° 5'	1° 53'	2 876	2 83
3	31° 18'	31° 42'	0° 14'	2 886	2 885
4	31° 42'	31° 42'	0°	2 887	2 887
5	34° 6'	31° 42'	- 2° 34'	2 815	2 924
6	36° 42'	31° 54'	- 5° 0'	2 799	2 855
7	38° 48'	32° 6'	- 6° 42'	2 784	2 860
8	40° 47'	32° 6'	- 8° 41'	2 787	2 885

glancing angle is less than the Bragg angle, the apparent shift of the Raman spot due to K β reflections merging with those of K α is taken into account in making the calculations. This shows that the phase-waves for the lattice vibration considered are perpendicular to the (100) and (110) planes. On the other hand, for the prismatic plane (211) which makes an angle of

$65^{\circ} 54'$ with 010 plane, the lattice spacing calculated using $\theta = 90^{\circ}$ shows a progressive diminution as the angle of incidence is increased. It remains fairly constant if we put $\theta = 65^{\circ} 54'$, as is only to be expected from the above-mentioned direction for the phase-waves. The lateral shift of the (211) Raman spot from the line joining the central and the Laue spots is also evidently connected with the azimuthal inclination of the phase-wave. The observations of the reflections from the (111) planes are neither sufficiently extensive nor sufficiently accurate to draw any conclusion regarding the phase-wave angle for those planes.

In conclusion the author desires to thank Sir C. V. Raman for his kind interest in the work.

Summary

The X-ray reflections from the (110), (200), (211) and (111) planes of hexamethyl-tetramine shows that the intensities of the dynamic reflections follow the same order as the intensities of the corresponding static reflections. The Raman spots of the crystal are relatively sharp compared to those from organic and inorganic crystals of complicated structure. These observations are readily explained by the fact that the molecular and the crystal structures of the substance have a high order of symmetry and that for the principal planes there is only one Raman X-ray active lattice vibration which corresponds to a movement of the two molecules against each other along the cube diagonal. The geometry and orientation of the spots are also found to depend on the direction of the phase-waves connected with the above vibration.

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FIG. 1

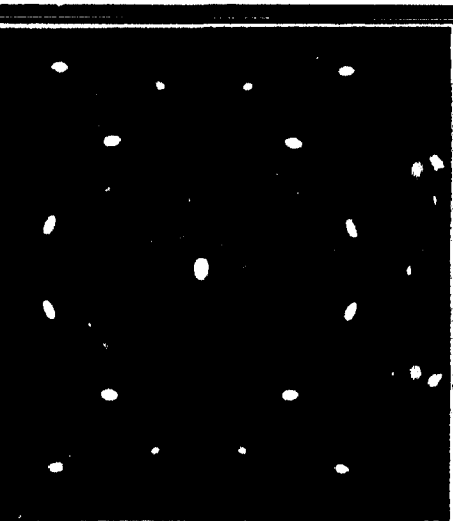


FIG. 2

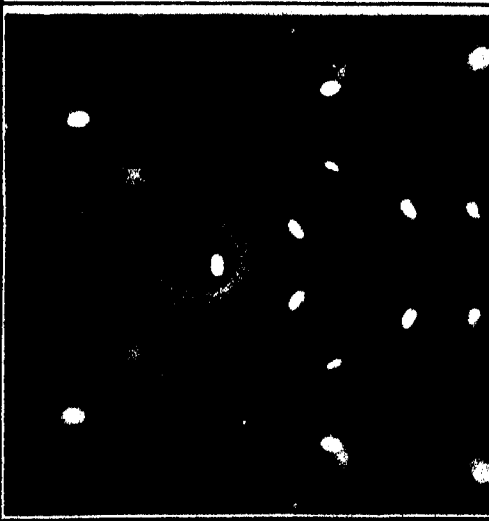
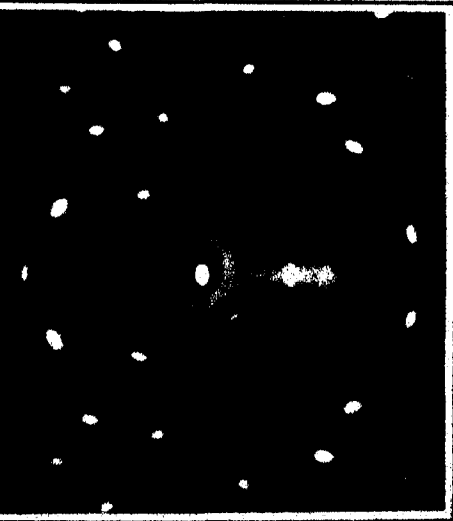
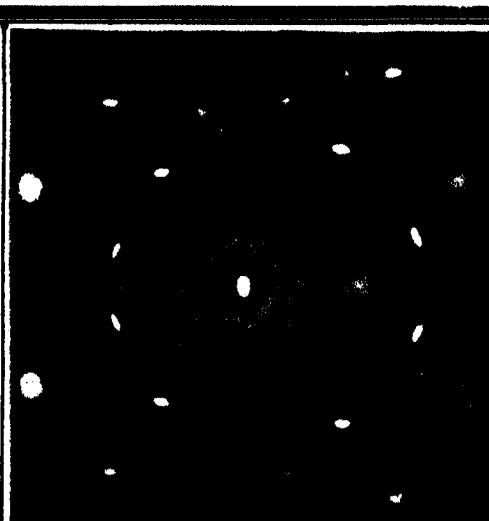


FIG. 3

FIG. 4

Raman X-Ray Reflections in Urotropin

FIG. 5

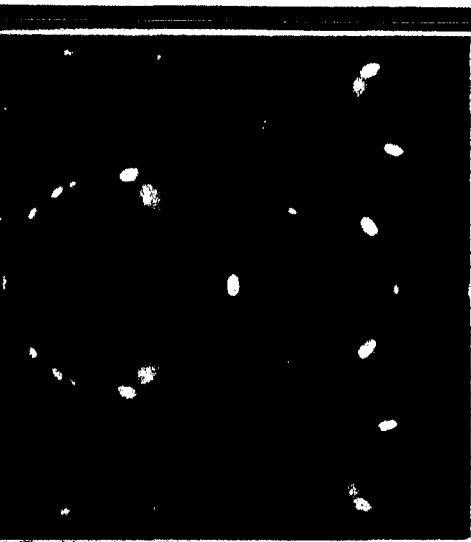


FIG. 6

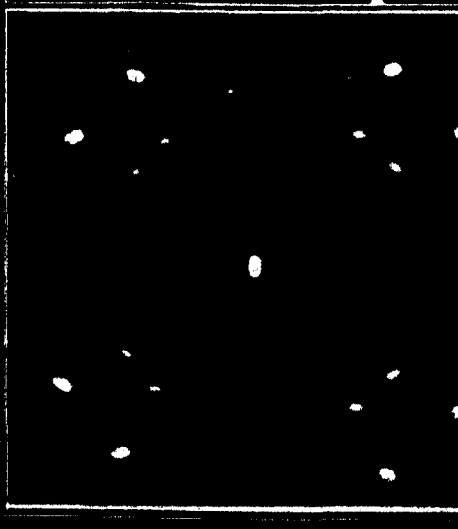
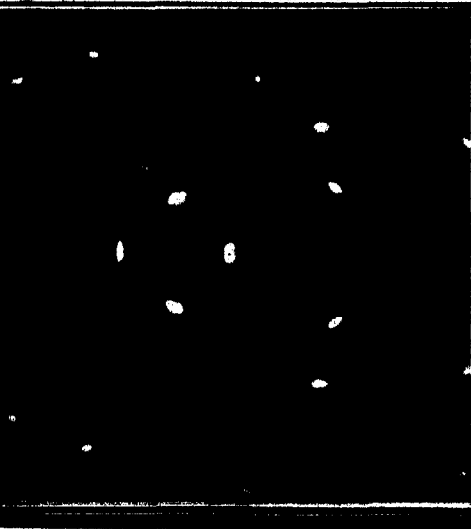
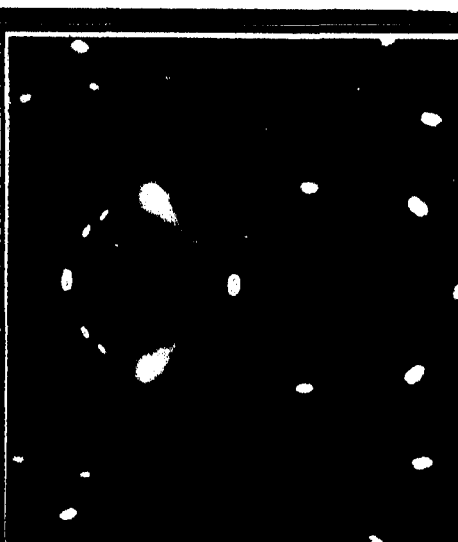


FIG. 7

FIG. 8

Raman X-Ray Reflections in Urotropin

X-RAY REFLECTIONS OF THE SECOND KIND IN METALLIC CRYSTALS

BY BISHESHWAR DAYAL

(From the Department of Physics Indian Institute of Science, Bangalore)

Received October 17, 1941

(Communicated by Prof Sir C V Raman, Kt, FRS, NL)

1 Introduction

THE nature of the metallic state is a problem of great theoretical and practical importance. The elementary nature of metals and the simplicity of their internal structure as revealed by X-ray studies entitle them to the first place in any general discussion on the solid state of matter. It is not surprising therefore that in the earliest discussions of one of the most important problems of the solid state—the nature of the thermal energy in crystals—the exponents of the various theories namely Einstein, Debye, and Born-K'arman, looked to the data obtained with metals for experimental support. About 36 of the metals crystallize in the cubic system, fifteen of them belong to the body-centred class, while eighteen of the rest have a face-centred close-packed structure which is geometrically one of the simplest arrangements of packing a large number of spheres in the densest possible manner. Because of this structural simplicity it was for a long time supposed that Debye's theory could be applied to all the metals of the above class without reserve, and that their vibrational spectrum could be replaced by that of an elastic continuum of which the upper limit was finite and so chosen as to make the total number of degrees of freedom also finite. The earliest work by Nernst and his school did appear to support this idea, but more accurate later determinations brought out numerous cases in which Debye's theory does not fit with the experimental results; while there are some so-called anomalous cases where Debye's theory completely breaks down. In two papers appearing in the November 1941 issue of these *Proceedings*, the author has examined these points in detail and has shown that all these difficulties of the specific heat theory find a very simple explanation in the fact that the vibrational spectrum of metallic lattices includes a number of discrete monochromatic frequencies which contribute Einstein terms to the specific heat formula. In the case of a face-centred cubic lattice, for example, the unit cube consists of four atoms

having twelve degrees of freedom. The three translations of the cell as a whole contribute terms of the Debye-type, while the remaining nine degrees of freedom are assigned to the Einstein frequencies which will in general be three triply degenerate ones.

Independent evidence for the presence of discrete monochromatic frequencies in solids can be obtained by the study of the new type of X-ray reflection discovered by Raman and Nilakantan (1940) in diamond and other crystals. They have shown that the incident X-ray quantum excites the infra-red monochromatic frequencies of the crystal lattice and thereby produces dynamic stratifications of electron density. The incident quantum is then reflected by these dynamic stratifications. The geometric direction of the resulting X-ray reflection is given by the formula of Raman and Nath (1940)

$$2d \sin \frac{\phi + \theta}{2} \sin \left(\vartheta + \frac{\phi - \theta}{2} \right) = n \lambda \sin \vartheta$$

where ϕ is the glancing angle of the Raman reflection, and θ the glancing angle of incidence with respect to the static crystallographic planes, while ϑ is the angle which the phase-waves make with the same static planes. It has been pointed out by these authors that the elastic waves of the Debye-type and the discrete Einstein vibrations would behave differently towards the incident quantum. The former would give rise to a general diffuse scattering with no pronounced maxima, while the latter would produce a distinct type of X-ray reflection. A study of the Raman reflection from single crystals of metals is therefore of great interest in providing a completely independent proof of the discrete frequencies in the vibrational spectrum of metals the presence of which is so strongly suggested by the specific heat considerations. From the temperature variation of the intensity of these reflections, it should be possible to evaluate the characteristic infra-red frequencies of metals as has actually been done by Dr. C. S. Venkateswaran for non-metallic crystals, as shown in an earlier paper in the present issue of these *Proceedings*.

In the present paper the author has investigated the Raman reflections from a number of planes of single crystals of aluminium for the various settings of the crystal. Some extra spots were observed by Preston (1939) in the Laue pictures of single crystals of this metal when the X-rays passed through a few standard directions in the crystal. He definitely discounted any idea of associating these spots with any lattice plane and ascribed them to diffraction by some limited groups of atoms. This idea however, is not acceptable (Born, 1941), and calculations with Preston's intensity formula

do not give the change in intensity which is actually observed when the orientation of the crystal is varied

2 Experimental Arrangements and Results

Single crystals of aluminium were prepared from a wire of pure metal about 1 mm in diameter by the stretch-anneal method (Carpenter and Elam, 1921). The orientation of the [110] direction in the crystals so prepared was generally found to be nearly parallel to the length of the wire. A Shearer-tube working at about 55 to 60 K V was used. The (200) Raman reflections were studied by using a molybdenum target and the other planes with a target made of silver. The period of exposure varied from 5 to 9 hours. On account of the ease with which the various planes could be studied by a simple rotation of the crystal about the goniometer axis, the crystal was so mounted that the [100] was nearly vertical. The orientation of the crystal was then adjusted in such a way that the Laue spot due to any desired plane was obtained very near the Bragg setting of the same plane for the monochromatic radiation of the material of the target. As should be expected, the Raman reflection for that plane is then observed by the side of the Laue spot. The new reflections were then photographed for various settings of the crystal about this position. The plate distance was measured separately for each position of the crystal by measuring its lateral shift in the field of view of a microscope as the crystal was rotated.

The results of measurement are given in the following tables. θ is the glancing angle of incidence, and ϕ the glancing angle of emergence with reference to the crystallographic plane given at the top of each table. 2ψ is the angle which the emergent ray makes with the incident ray while d is the spacing calculated from the Raman-Nath formula (given earlier in this paper) with the assumption that the angle $\delta = 90^\circ$.

TABLE I

(200) Raman reflections from single crystals of Al for Mo K_α
Theoretical $d = 2.023 \text{ \AA}$ $\delta = 90^\circ$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
12°-28'	20°-3'	7°-35'	4°-53'	2.04
11°-32'	20°-10'	8°-38'	2°-54'	2.03
11°-17'	20°-6'	8°-49'	2°-28'	2.04
10°-21'	20°-13'	9°-52'	29'	2.02
8°-28'	20°-10'	11°-42'	-(3°-14')	2.01
6°-52'	19°-54'	13°-2'	-(6°-10')	2.06
5°-32'	20°-9'	14°-37'	-(9°-5')	2.04

TABLE II

(111) Raman reflections for Ag K_{α} from single crystals of Al
Theoretical $d = 2.336 \text{ \AA}$ $\vartheta = 90^{\circ}$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
4°-43'	13°-36'	8°-53'	-(4°-10')	2.37
6°-32'		not separated from Laue spot		
7°-31'				
9°-6'	13°-43'	4°-37'	4°-29'	2.34
9°-13'	13°-33'	4°-20'	4°-53'	2.37
10°-2'	13°-41'	3°-39'	6°-23'	2.35
10°-33'	13°-33'	3°-0'	7°-33'	2.38
10°-55'	13°-38'	2°-43'	8°-12'	2.37
11°-31'	13°-46'	2°-15'	9°-16'	2.34
12°-6'	13°-38'	1°-32'	11°-34'	2.37
12°-50'	13°-38'	0°-48'	12°-2'	2.37

TABLE III

(220) Raman reflections for Ag K_{α} from single crystals of Al
Theoretical $d = 1.43 \text{ \AA}$ $\vartheta = 90^{\circ}$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
6°-40'	22°-31'	15°-51'	-(9°-11')	1.44
8°-59'	22°-24'	13°-25'	-(4°-26')	1.44
12°-4'		not separated from Laue spot		
12°-18'	22°-36'			
13°-23'	22°-32'	10°-18'	2°-0'	1.43
15°-24'	22°-47'	9°-9'	4°-13'	1.43
		7°-23'	8°-1'	1.42

TABLE IV

(222) Raman reflections from single crystals of Al for Ag K_{α}
Theoretical $d = 1.168 \text{ \AA}$ $\vartheta = 90^{\circ}$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
11°-31'	27°-31'	16°-8'	4°-37'	1.18
12°-32'	27°-31'	14°-59'	2°-17'	1.18

3 Discussion

The spacings calculated from the Raman-Nath formula for $\vartheta = 90^{\circ}$ agree very well with the known crystal spacings given at the top of each table. The accuracy of the present measurements is limited for two main reasons. In the first place in order to avoid the large absorption of the Cu K_{α} radiations, shorter wave-lengths had to be used; secondly the continuous radiation present gave rise to streaks which made the exact determination of the position of the Raman spot slightly difficult, particularly in positions when its separation from Laue spots was the largest. Nevertheless it can be stated that the angle between the crystallographic planes

studied and the phase-waves probably did not differ by more than ten degrees from the value ($\vartheta = 90^\circ$) given above. This is shown by the fact that if we calculate the spacings by putting $\vartheta = 80^\circ$, the largest difference between the spacings so calculated and those given in the column 5 of the above tables is about 2% in the case of (111) and (220) reflections and about 1% in the case of 200 ones.

The most remarkable feature about these reflections is that they are fairly sharp and not so diffuse as would be the case if they were due to diffuse scattering. The essential difference between them and the Laue spots seems to be that the boundary of the former is not quite as sharp as in the latter. The angular width of the new spots does not change very much with their position relative to the Laue spots, and appears to be largely governed by the size of the pin hole used in the camera.

The above facts seem to leave no doubt that we are dealing with a regular reflection and not with any diffuse scattering. Brindley and Ridley (1938) have given the atomic structure factors of the various planes of aluminium in the following order (of decreasing magnitude) 111, 200, 220 and 222. The same order of intensity appears with the new reflections.

In conclusion the author wishes to express his thanks to Sir C. V. Raman, Kt, FRS, NL, for the interest he has taken in the work and to Dr P. Nilakantan for help in the experimental work.

4 Summary

The presence of discrete Einstein frequencies in metals which is suggested by the observed deviations from the Debye specific heat formula finds support in the fact that the various lattice planes of aluminium show strong Raman reflections. The (200), (111), (220) and (222) Raman reflections from single crystals of aluminium have been studied for a large number of settings of the crystal. It has been shown that the position, sharpness and the angular width of the new spots point to their being a new type of reflection and not diffuse maxima of X-ray scattering. The positions of the spots indicate that the angle between the crystallographic planes and the phase waves does not differ very much from 90° .

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THE LATTICE SPECTRUM AND THE RAMAN X-RAY REFLECTIONS BY ROCK-SALT

BY DR C S VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

It has been shown in an earlier paper that the diffuse maxima observed by several authors in the Laue patterns of rock-salt are due mainly to the dynamic X-ray reflections by the monochromatic crystal vibrations as was originally explained by Raman and Nilakantan¹ (1940). In the present paper it is proposed to give an analysis of the lattice vibrations of the sodium chloride crystal and ascertain their part in determining the intensity and the geometric law of the Raman X-ray reflections from its principal planes

2 Group Theory and the Lattice Spectrum of Rocksalt

The unit cube of the rock-salt lattice contains four sodium and four chlorine atoms, each group possessing tetrahedral symmetry. The co-ordinates of the atoms are

Na $0, 0, 0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, 0, \frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}$

Cl $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0, 0, 0, \frac{1}{2}, 0, 0, 0, \frac{1}{2}$.

There are twenty-four degrees of freedom for the atoms in the unit cell. The crystal vibrations may be classified among the different symmetry classes of the space group O_h to which the crystal belongs, according to the following character table. The notations employed are the same as those given by Placzek² and the procedure followed in drawing up the table is the same as that given by Bhagavantam and Venkatarayudu³ (1939). It will be seen from Table I that there are altogether eight modes of vibrations for the crystal all of which are triply degenerate. One of these in class F_{2u} corresponds to the translations of the unit as a whole along the three axes and may, for the present, be assigned to the Debye elastic spectrum.

Of the remaining seven, two belonging to the class F_{1u} are active in infra-red and inactive in Raman, and five in class F_{2u} are inactive in both. One of the former class corresponds to the oscillation of the sodium lattice against the chlorine lattice, and is referred to in the following as inter-lattice vibration. The remaining one of this class and one of F_{2u} correspond to the

TABLE I
Character Table for Rock-salt

O _h	E	8 C ₂	3 C ₂	6 σ	6 S ₄	i	8 S ₆	3 σ	6 C ₂	6 C ₄	n _i	Raman	Infra-red
A _{1g}	1	1	1	1	1	1	1	1	1	1	0		
A _{2g}	1	1	1	-1	-1	1	1	1	-1	-1	0		
E _g	2	-1	2	0	0	2	-1	2	0	0	0		
F _{1g}	3	0	-1	-1	1	3	0	-1	-1	1	0		
F _{2g}	3	0	-1	1	-1	3	0	-1	1	-1	0		
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	0		
A _{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	0		
E _u	2	-1	2	0	0	-2	1	-2	0	0	0		
F _{1u}	3	0	-1	-1	1	-3	0	1	1	-1	2	f	Active
F _{2u}	3	0	-1	1	-1	-3	0	1	-1	1	6	f	Inactive
u _R	8	2	8	4	4	8	0	8	4	4			
ψ _f	24	0	-8	4	-4	-24	0	8	-4	4			
h _f ψ _f	24	0	-24	24	-24	-24	0	24	-24	24			

'breathing' oscillations of sodium and chlorine atoms in the unit, in one of which all the atoms move in the same phase (symmetric), and in the other the movements of the sodium and the chlorine atoms are opposite in phase (anti-symmetric). The author will go more fully into the vibrational spectrum of the crystal in a subsequent paper.

3 The Dynamic Reflections of X-rays by Rock-salt

The displacements of the atoms in the inter-lattice vibration are normal to the (100) planes and those of the 'breathing' oscillations are normal to the (111) planes. As a first approximation, we consider the effect of these three modes of vibrations on the intensities of Raman X-ray reflections. The other modes of vibrations would contribute only relatively feeble components normal to (100), (111) and (110) planes. If *a* and *b* are the amplitudes of the Na and Cl atoms in the direction of vibration, the co-ordinates of the eight atoms for the three vibrations are

1. for the anti-symmetric

$$\begin{aligned} \text{Na} & \cdot \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}, \frac{1}{2} - \frac{a}{\sqrt{3}}, \frac{1}{2} - \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}, \text{ etc} \\ \text{Cl} & \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{1}{2} - \frac{b}{\sqrt{3}}, -\frac{b}{\sqrt{3}}, -\frac{b}{\sqrt{3}} \text{ etc} \end{aligned}$$

2. *for the symmetric*

Na : Same as for 1

$$\text{Cl } \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{1}{2} - \frac{b}{\sqrt{3}}; \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{b}{\sqrt{3}}, \frac{b}{\sqrt{3}} \text{ etc.},$$

and 3 *for the interlattice, considering its triple degeneracy*Na $a', a', a', \frac{1}{2} + a', \frac{1}{2} + a', a', \text{ etc}$ Cl $\frac{1}{2} - b', \frac{1}{2} - b', \frac{1}{2} - b', \frac{1}{2} - b', -b', -b' \text{ etc}$

Sir C V Raman has given the following expressions for the intensities of static (I_B) and dynamic (I_R) X-ray reflections at or very near the Bragg setting. For an imperfect crystal,

$$\sqrt{I_B} = \sum_p J_0(\zeta_p) f_p' \cos(2\pi \nu t - z_p) \quad \text{I}$$

$$\sqrt{I_R} = \sum_p J_1(\zeta_p) f_p' \sin[2\pi(\nu \pm \nu^*)t - z_p] \quad \text{II}$$

where $\zeta_p = \frac{2\pi \xi_p}{d}$, ξ_p being the component of the displacement of the p th atom normal to the crystal plane considered and d its lattice spacing. For an infra-red vibration of frequency ν^* , the amplitude a_p is given by $\sum_p \frac{1}{2} m_p a_p^2 = \frac{h}{4\pi^2 \nu^*}$ where m_p is the mass of the atom. The dynamic structure amplitude of any plane is then given by

$$|F|^2 = [\sum_p J_1(\zeta_p) f_p' \cos 2\pi N(hx_p + ky_p + lz_p)]^2 + [\sum_p J_1(\zeta_p) f_p' \sin 2\pi N(hx_p + ky_p + lz_p)]^2 \quad \text{III}$$

where h, k, l are the Miller indices of the plane, N is the order of reflection and x_p, y_p and z_p are the co-ordinates of the *displaced* atom. These expressions for the 1st and 2nd order reflections by the 111, 100 and 110 planes have been deduced for the three modes of vibrations. And assuming that the frequencies of these vibrations are all in the neighbourhood of 160 cm^{-1} and remembering that they are triply degenerate, the amplitude a_p is calculated for the three cases and hence the corresponding $\xi_p, \zeta_p, J_0(\zeta_p)$ and $J_1(\zeta_p)$ for Na and Cl atoms separately in each case. Substituting these values in the expressions for intensities, we get the following table for the intensities of the static and dynamic reflections.

The data given in Table II lead to the following conclusions (1) The intensities of the dynamic reflections from (222), (200) and (220) planes are proportional to the corresponding Bragg intensities. (2) The (100) and (110) dynamic reflections should appear weakly whereas their static reflections are forbidden. The dynamic structure amplitude of (100) reflections is sufficiently

TABLE II
Intensities of Raman and Bragg X-ray Reflections

Mode of Vibration	Intensities $ F ^2$	MILLER INDICES OF PLANES					
		111	222	100	200	110	220
Anti-Symmetric	Raman	11	17 7	003	43 8	9×10^{-5}	27 6
	Bragg	310	2700	0	6624	0	4020
Symmetric	Raman	11	17 7	045	43 8	9×10^{-5}	27 6
	Bragg	310	2700	0	6624	0	4020
Inter-Lattice	Raman	21	5 5	0	14 2	0	8 6
	Bragg	310	2700	0	6600	0	4000
	Raman (Total)	43	40 9	0453	101 8	18×10^{-5}	63 8
	Raman Bragg	$\frac{1}{720}$	$\frac{1}{66}$		$\frac{1}{66}$		$\frac{1}{63}$

high (about 5×10^{-3}) to record the spot in well-exposed pictures (3) The intensity of the (111) dynamic reflections is only $1/720$ of the static reflections, while that of (222) is $1/66$. As the Bragg intensities of (111) to (222) reflections are in the ratio 3 11, the corresponding ratio for the Raman intensities is 1 40.

4 Experimental Results

Figs 1-4 in the accompanying Plate are four photographs taken with a crystal of rock-salt set with one of the (111) planes normal to X-rays and then rotated about [110] axis. Fig 1 shows the trigonal symmetry, when the X-rays are nearly normal to the plane and the glancing angle on (111) planes measured from their Laue spots is $19^\circ 36'$. Figs 2-4 are taken with X-rays making glancing angles of $11^\circ 32'$, $4^\circ 46'$ and nearly $2^\circ 30'$ with the 111 plane. On account of the great thickness of the crystal traversed by X-rays due to oblique incidence, the absorption is great and it was observed that the effective X-ray wave-length maximum is 0.46 \AA . The corresponding Bragg angle for the first order of (111) reflection is $3^\circ 40'$ and for the second order is $7^\circ 37'$. The strong Raman spot of the (222) reflections may be seen in all pictures. On the other hand, the (111) Raman spot appears very weakly only in Fig 4 in which it is very near the Bragg setting. In Fig. 3, the (111) reflection is nearer to the Laue spot than the (222) reflection and yet it is not recorded while the latter comes out with great intensity. The investigation thus clearly shows that the first order of the dynamic reflection by the (111) plane is

extremely weak which is in qualitative agreement with the theoretical calculations. These results again demonstrate that the new spots in rock-salt do not owe their origin to the scattering of X-rays by the elastic waves, for which the relative intensities of the first and second order maxima should be nearly* of the same order as of the Bragg Reflections, viz., 3 : 11. The (222) Raman spots show also a drift towards the Laue spot as the crystal is rotated.

5 Phase-waves and the Geometric Law of the Raman X-ray Reflections

It may be reasonably assumed that the phase waves associated with the lattice vibrations of rock-salt will be parallel to the planes containing only either sodium atoms or chlorine atoms. Secondly the phase-waves responsible for the Raman spot lying approximately on the line joining the central and the Laue spots, should be one having the minimum azimuthal angle. From these two considerations it is assumed that the phase-waves will be parallel to the {311} planes. There are altogether twenty-four planes belonging to this "form". The geometric law of the dynamic reflections is given by Raman and Nath⁵ (1940) as $2d \sin \frac{\theta + \phi}{2} \sin \left(\vartheta - \frac{\phi - \theta}{2} \right) = \lambda \sin \vartheta$, where d is the lattice spacing, θ is the glancing angle of incidence, $\theta + \phi$, the angle between the incident and reflected rays, ϑ is the angle made by the reflecting plane with one of the {311} planes.

Jauncey and Baltzer⁶ (1941) have shown by an elegant experimental method that the diffuse maxima of the (400) and (620) planes drift towards the Laue spot as the crystal is rotated. In order to verify their data, the author has reinvestigated the case of rock-salt with Mo radiations, using a fine aperture lead-slit and a thin crystal and taking care in setting the crystal so that the plate distance remains constant for all crystal orientations. It was observed that the dynamic reflections for the 200, 400, 220 and 440 planes for Mo K α do not show any measureable drift from the Bragg position, as is only to be expected from the above formula. Since no shift has been noticed the measurements are not given here. The extrapolated data furnished by Zachariasen⁷ (1941) from a re-measurement of the reproduced photographs of Raman and Nilakantan (1940) are thus unjustifiable and are indeed contradicted by his own rigorous formula given later (Zachariasen⁷, 1941).

In Tables III-V, the results of Jauncey and Baltzer⁶ are given along with those of the present author. The readings in the neighbourhood of the Bragg

* According to Zachariasen's rigorous formula⁴ (1941) the intensity varies as $1/\cos^2 \theta_B$ for small values of $\theta, -\theta_B$. This gives an increase of only 1.4% for the second order reflection over the first order.

angle are omitted The phase-wave angle, $l e$, the angle made by the reflecting plane with one of the $\{311\}$ planes, in each case is shown in the beginning of each table

TABLE III

$$\vartheta = 72^\circ 27' = 100 \wedge 113$$

(400) reflection $d=2.81\text{\AA}$ Jauncey CuK_α				(600) reflections $d=2.81\text{\AA}$ Author MoK_α			
2θ	$\theta + \phi$	$\phi - \theta$	d	2θ	$\theta + \phi$	$\phi - \theta$	d
$80^\circ 14'$	$68^\circ 38'$	$-11^\circ 36'$	2.831	$39^\circ 12'$	$44^\circ 14'$	$5^\circ 2'$	2.8
$78^\circ 14'$	$68^\circ 38'$	$-9^\circ 36'$	2.810	$46^\circ 12'$	$44^\circ 31'$	$-1^\circ 41'$	2.82
$76^\circ 14'$	$68^\circ 20'$	$-7^\circ 54'$	2.805	$50^\circ 8'$	45°	$-5^\circ 8'$	2.82
$74^\circ 14'$	$67^\circ 50'$	$-6^\circ 24'$	2.809	$54^\circ 20'$	$45^\circ 24'$	$-8^\circ 56'$	2.83
$72^\circ 14'$	$67^\circ 32'$	$-4^\circ 42'$	2.803				
$60^\circ 14'$	$65^\circ 2'$	$+4^\circ 48'$	2.825				
$58^\circ 14'$	$64^\circ 26'$	$+6^\circ 12'$	2.840				
$56^\circ 14'$	$64^\circ 26'$	$+8^\circ 12'$	2.830				

TABLE IV

$$\vartheta = 55^\circ 6' = 311 \wedge 130$$

$$(620) \text{ reflections } d = 89\text{\AA}$$

Jauncey CuK_α				Author MoK_α			
2θ	$\theta + \phi$	$\phi - \theta$	d	2θ	$\theta + \phi$	$\phi - \theta$	d
$126^\circ 8'$	$123^\circ 54'$	$-3^\circ 14'$	889	$43^\circ 51'$	$46^\circ 28'$	$2^\circ 37'$	884
$125^\circ 8'$	$122^\circ 36'$	$-2^\circ 32'$	890	$50^\circ 45'$	$47^\circ 21'$	$-3^\circ 24'$	900
$113^\circ 8'$	$115^\circ 36'$	$2^\circ 28'$	894	$52^\circ 46'$	$47^\circ 41'$	$-5^\circ 5'$	904
$111^\circ 8'$	$114^\circ 54'$	$3^\circ 46'$	891				
$109^\circ 8'$	114°	$4^\circ 52'$	890				

TABLE V

 $\phi = 82^\circ 15' = 13T \wedge 201$, *X-ray wave-length* $\cdot 708 \text{ \AA}$ (402) reflections Lattice Spacing $\approx 1.26 \text{ \AA}$

2θ	$\theta + \phi$	$\phi - \theta$	d
$25^\circ 58'$	$32^\circ 17'$	$6^\circ 19'$	1.267
$35^\circ 24'$	$32^\circ 33'$	$-2^\circ 59'$	1.272
$41^\circ 24'$	$32^\circ 49'$	$-8^\circ 35'$	1.275
$45^\circ 46'$	$33^\circ 5'$	$-12^\circ 41'$	1.271
$47^\circ 10'$	$33^\circ 5'$	$-14^\circ 25'$	1.276
$49^\circ 50'$	$33^\circ 20'$	$-16^\circ 20'$	1.273

Considering the limitations for accurate experimental measurements, Tables III, IV and V show that the lattice spacing obtained in every case is fairly constant and nearly equal to the theoretical value. It may be remarked here that as has been indicated by some authors, the geometric law for the new reflections is more or less similar whether they are considered as arising from the infra-red vibrations (Raman), elastic waves (Faxén-Waller-Zachariasen), or mosaic blocks (Preston-Bragg⁶). As such, any agreement between the theoretical and experimental values (see also Zachariasen⁹, 1941) cannot be regarded as being in favour of one or other of these theories. Indeed, the present study shows that the geometric behaviour of the Raman reflection gives us a valuable method of determining the direction of the phase-waves in the crystal.

6 Origin of the Streamers in the Rock-salt Patterns

The Laue photographs of rock-salt reproduced by Raman and Nilakantan (1940) show that many of the quantum reflections have faint streamers running in different directions associated with them. These are also clearly seen in the pattern obtained by Gregg and Gingrich (1940) using monochromatic radiations, an original print of which kindly sent by them to Sir C. V. Raman was placed at the disposal of the author. These streamers have obviously a similar origin to those recorded by Raman and Nilakantan (1940) for diamond and explained in a complete fashion by Pisharoty (1941) on the assumption that associated with each of the (111) planes there are three phase waves parallel to the (100) planes. In the case of rock-salt the (311) planes take the place of the (100) planes of diamond. Calculations made on the lines indicated by Pisharoty for diamond and taking three (311) phase-waves symmetrically situated with respect to the reflecting plane shows that the angle between streamers connected with (220) and (402) planes lies between 80° and 85° . Observations made on the photograph furnished by Dr. Gingrich are in

FIG. 1

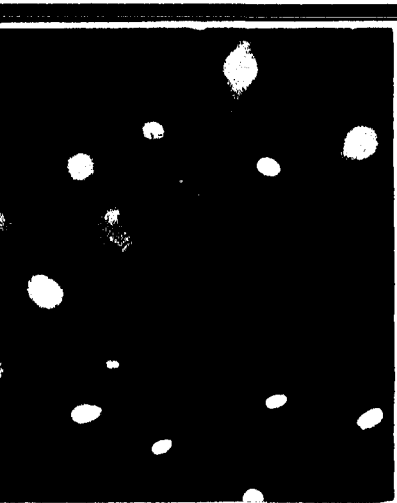


FIG. 2

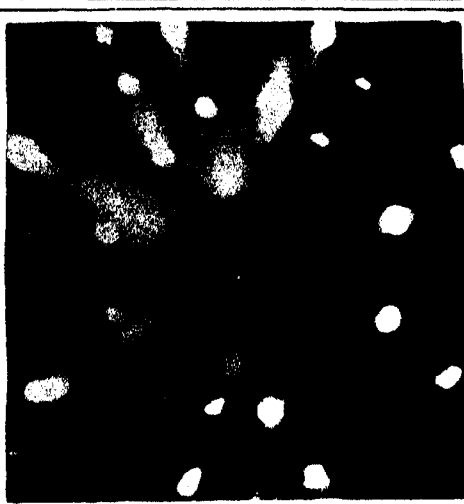
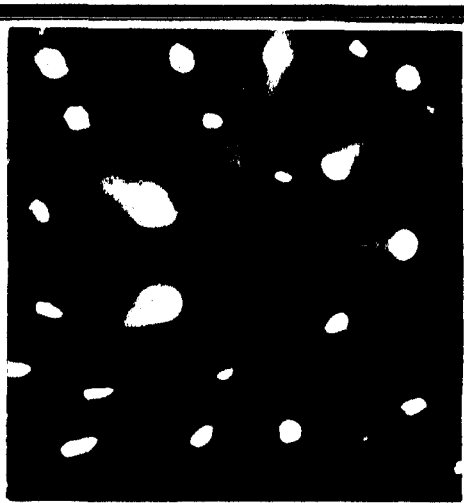


FIG. 3

FIG. 4

agreement with this calculation. It is also possible that the cross-streamers connecting the 'maxima' are due to the combined effect of different phase-waves and require further careful consideration. A faint spot corresponding to 100 reflection is also discernible in the latter photograph and if substantiated by observations on the original negative would confirm the theoretical expectation made earlier in the paper.

In conclusion I take this opportunity to thank SRI C. V. RAMAN, I.R.S., for his continued interest in my work. The author's thanks are also due to Mr. Rama Pisharoty for some discussions he had with him in the calculation of intensities.

7 Summary

The lattice vibrations of rock-salt are analysed and the intensities of the first and the second orders of the Raman X-ray reflections from the (111), (100) and (110) planes are calculated for the three principal modes of vibration. These calculations show that the intensities of the (222), (200) and (220) Raman reflections are proportional to those of their corresponding Bragg reflections. The intensity of the (111) Raman reflection is only 1/40 of that due to (222) whereas the ratio of the corresponding Bragg reflections is 9/33. This is in agreement with experimental observations with rock-salt. The (100) and (110) Raman reflections should be very weak. The drift of the Raman spot observed by Jauncey and Baltzer for 400 and 620 and also by the present author for 600, 620 and 420 planes for different crystal orientations is satisfactorily explained on the assumption that the phase-waves are parallel to {311} planes of the crystal. The 'streamers' that are observed in association with the 'maxima' in rock-salt are also explained on the basis of the co-existence of at least three such waves effectively connected with any particular plane.

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THE ABSOLUTE INTENSITY OF THE RAMAN X-RAY REFLECTIONS IN DIAMOND

BY P RAMA PISHAROTY

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

IN an earlier paper appearing in this issue of the *Proceedings*, the author has shown how the dynamic structure amplitude of any lattice spacing of diamond may be calculated for the 1332 cm^{-1} oscillation† The Planck oscillator of this frequency ν^* is taken to consist of two atoms and the amplitude of the oscillation is calculated by giving an energy $h\nu^*$ to each oscillator All the oscillators are assumed to be in phase, so that we get the structure amplitude of the Raman or quantum reflection at the correct Bragg setting only We add the *periodic* displacements of the various atoms of the unit cell to their static co-ordinates and substitute the vectorial sums, for the respective co-ordinates x_p, y_p, z_p , of the p th atom of the unit-cell, in the following expression for the structure amplitude of the reflection from the (hkl) plane

$$F_{hkl} = \sum_p f_p e^{2\pi i (h x_p + k y_p + l z_p)} e^{2\pi i \nu t}$$

Here f_p is the atomic scattering factor of the p th atom and ν is the frequency of the incident X-radiation The (hkl) plane would be active for the Raman

TABLE I

Indices of the plane	Spacing in A U	Classical or Bragg reflection	Quantum or Raman reflection	Indices of the plane	Spacing in A U	Classical or Bragg reflection	Quantum or Raman reflection
111	2.058	A	A	400	0.889	A	F
311	1.073	A	A	420	0.795	F	A
331	0.817	A	A	422	0.726	A	F
333	0.685	A	A	440	0.629	A	F
335	0.542	A	A	620	0.562	A	F
551	0.498	A	A	622	0.537	F	A
				660	0.419	A	F
200	1.778	F	A	662	0.409	F	A
220	1.258	A	F	844	0.363	A	F
222	1.029	F	A				

A—Allowed

F—Forbidden

† Recently Nayar has found that there are discrete lattice frequencies for diamond as low as 127 cm^{-1} . They are not discussed here since their modes of oscillation are not as yet known. It is possible that some of them may be active where the quantum reflections for the 1332 oscillation is forbidden. These quantum reflections, if any, would be then more temperature-sensitive.

reflection whenever there is a term with frequency ($\nu \pm \nu^*$) in the reflected radiation. The above table gives the active planes for the quantum reflection produced by the lattice oscillation of 1332 cm^{-1} . The first series of planes have all their indices *odd* and every one of them is allowed for the Raman reflections. When all the indices are *even*, the Raman reflections are 'forbidden' if $h + k + l = 4n$, and are 'allowed' if $h + k + l = 4n + 2$, the Bragg reflection being 'forbidden' for the latter case. A face-centred cubic lattice has planes in common with the diamond lattice which are 'forbidden' for the classical reflections. All of them are 'forbidden' for the quantum reflections as well.

The author has calculated in his previous paper already mentioned, that the intensity of the Raman reflection for the (111) planes of diamond in the correct Bragg setting would be about 7% of the total reflected intensity. The experiments of Raman and Nilakantan¹ showed that the intensity of the quantum reflection is fairly large when close to the Bragg setting, and that it falls off rapidly as the setting is continuously altered. But they have given no quantitative data and have not approached very close to the Bragg setting. The present paper gives an account of an experimental determination of the absolute intensity of the quantum reflections from the (111) planes, in terms of the intensity of the direct monochromatic beam.

2 Experiments and Results

Copper X-radiations generated in a Siefert tube of the demountable type, worked at 56 k v peak and 22 ma, was passed through a lead slit 0.2 mm wide, 4 mm high, and 130 mm deep. The emergent narrow pencil was monochromatised by reflection at the octahedral cleavage face of a thin plate of diamond ($10 \times 6 \times 0.8\text{ mm}^3$) set at the Bragg angle of the K_α radiation. The reflected beam was easily visible on a fluorescent screen, held beyond a second slit 0.2 mm wide and 2 mm high, cut in a sheet of lead, and placed at a distance of 2 cm. from the crystal.

The monochromatic beam, coming through the second slit, passed through a second crystal of diamond (0.8 mm thick), set with its octahedral cleavage face nearly normal to the incident beam. A rod of 10 cm length attached to the goniometer of this crystal enabled it to be turned through small angles. A plane mirror attached to the goniometer was used together with a scale and telescope to measure small angular displacements of the crystal. A millimetre shift on the scale corresponded to a shift of the crystal through 1.3 minutes of arc.

After a series of trials, the second crystal was set to give Bragg reflection from the interior (111) planes, as registered on a photographic film kept

normal to the direct beam and at a distance of 4.5 cm from the crystal. The crystal was rotated through known angles from this position, and the corresponding quantum reflections were recorded. In each case the direct beam was allowed to be incident on the film all the time, but with its intensity reduced to a known fraction by the interposition of a definite number of thin standard nickel foils supplied by the firm of Adam Hilger. Each foil was 0.033 mm thick. The number of foils were adjusted so that the direct spot and the quantum reflection recorded on the same film were of comparable intensities. Up to five foils were used in the experiments.

A density-log intensity curve, for the Kodak "Duplitzed" X-ray films used, was drawn employing the step-wedge method of Baltzer and Nafe², with the incident X-rays nearly monochromatised by a nickel filter 0.066 mm thick. All the films were developed with the same stock of developer under the same conditions of time and temperature. A Moll microphotometer supplied by Kipp and Zonen was employed for the photographic density determinations.

Measurements were taken only up to thirty minutes of arc from the Bragg setting by this method. The time of exposure for this setting was ten hours. For wider settings of the crystal monochromatisation was dispensed with, as very long exposures were required. A narrower slit was employed and the beam directly passed through the second crystal. Raman reflections for half-a-degree and one degree off the Bragg setting were recorded on the same film, one below the other, and with suitable exposures to make both of them nearly of the same photographic density. Similarly, the quantum reflection when $(\theta_B - \theta) = 2^\circ$ was compared with the one for which $(\theta_B - \theta) = 1^\circ$. The actual intensities were compared by assuming the value of the exponential of time, in the expression for the photographic density produced by X-rays, to be one.

The following table gives the intensities of the quantum reflections, for various settings of the crystal, as fractions of the intensity of the direct beam.

TABLE II

$2(\theta_B - \theta)$	$\frac{\text{Intensity of the Raman reflection}}{\text{Intensity of the direct beam}}$
5' 2	0.010
10' 4	0.0029
18'	0.00085
20'	0.00028
1° 2'	0.0000020
2° 0'	0.0000004
4° 0	0.00000008

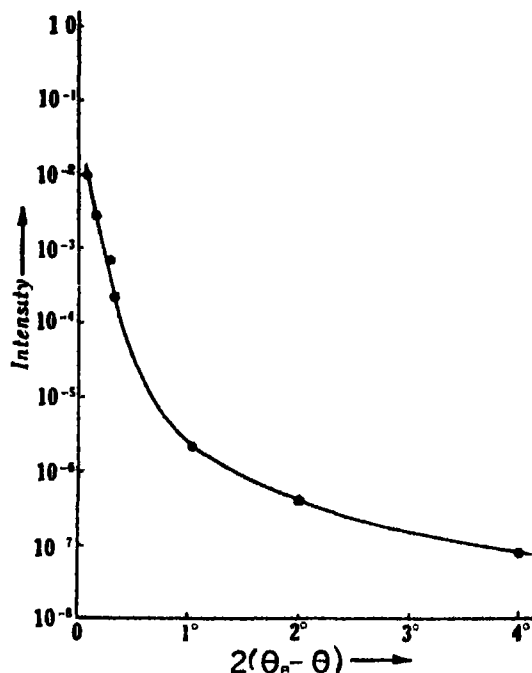


FIG 1

Graph of Intensity against Crystal Setting

The results are plotted in Fig 1, the ordinates being the intensities and the abscissæ being twice the difference between the Bragg angle θ_B and the glancing angle θ . It can be shown from the Raman and Nath formula³ that,

$$2(\theta_R - \theta) \simeq 2 \frac{d \cos(\theta_B + \vartheta)}{\Delta \cos \theta_B}$$

where d is the crystal spacing, Δ is the phase-wave-length of the lattice oscillations, and ϑ is the inclination of the phase-waves to the lattice spacings. Hence, the curve represents the variation of the intensity of the quantum reflections with the reciprocal of the phase-wave-length of the lattice oscillations involved.

The natural divergence of the beam is determined by the width of the second slit and the far end of the first slit. This works out in the present experiment to be about four minutes of arc on either side of the central beam. To this is to be added the divergence of the Bragg reflection. But this is of the order of a few seconds of arc, for a perfect crystal of diamond, and hence negligible. Therefore there can only be some doubt about the accuracy of the first value in the above table.

3 Discussion

It is found that the intensity of the Raman reflection does approach a few hundredths of that of the incident beam and therefore, of the Bragg reflection itself. This is in general agreement with the theory, which indicates an intensity of about 7% of the Bragg reflection in the most favourable setting. The intensity of the quantum reflection falls with extreme rapidity at first and then more slowly with increase of the value of $(\theta_B \sim \theta)$, or from another point of view, with decrease of the operative phase-wave-length of the lattice oscillations. The facts thus suggest that, in diamond, the lattice oscillations with long phase-wave-lengths are far more probable than those with smaller phase-wave-lengths.

My sincere thanks are due to Sir C. V. Raman, F.R.S., for his invaluable help during the course of this work.

4 Summary

The lattice planes of diamond which are 'allowed' and 'forbidden' for the Raman reflections produced by the lattice oscillation of 1332 wave-numbers are tabulated. The intensity of the quantum reflections from the (111) planes are directly compared with the incident monochromatised X-rays, at settings ranging from a few minutes of arc to two degrees away from the Bragg setting. The results show that the intensity of the Raman reflection at the closest setting is a few hundredths of the intensities of the incident beam, in general agreement with the theoretically estimated value of 7% at the exact Bragg setting. The intensity falls off rapidly at first and then more slowly as the crystal setting is continuously altered. When the angle of incidence differs by two degrees from the Bragg value, the intensity is roughly a ten-millionth part of the incident beam.

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ON THE MULTIPLE SPOTS AND STREAMERS EXHIBITED BY THE (111) DYNAMIC REFLECTIONS IN DIAMOND

BY P RAMA PISHAROTY AND R V SUBRAHMANYAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE experiments of Raman and Nilakantan¹ on the quantum reflection of X-rays from the (111) planes of diamond have definitely established that the phase-waves of the lattice oscillations, excited by the incident X-rays are parallel to the (100) planes transverse to the plane of incidence. The present paper deals with an experimental study of the effects of the other two possible sets of phase-waves parallel to the cube faces, on the Raman reflections. One of us has shown in a previous paper² that these sets of phase-waves also would give rise to weaker Raman reflections, in directions considerably out of the plane of incidence of the X-rays on the static spacings. In fact, the streamers and the subsidiary spots accompanying the main Raman reflection (Raman and Nilakantan, 1940) are quantum reflections arising from the dynamic stratifications produced by the combination of these waves with the static (111) spacings.

2. Experimental

A Siefert tube of the demountable type with a copper anti-cathode, run at 56 k v peak and 22 ma was the source of X-rays. The horizontal X-ray beam was passed through a lead slit of the pin-hole type of effective depth 95 mm and diameter 1 mm. The emergent pencil had a divergence of 72'. This narrow pencil was then passed through a thin triangular plate of diamond, cut nearly parallel to a set of (111) planes and held nearly normal to the incident beam. The subsidiary phenomena accompanying the main Raman reflection were studied for angles of incidence close to the Bragg angle corresponding to the (111) planes of diamond and the Cu K_α radiation.

The crystal was set initially so that the incident plane was a plane of symmetry parallel to a (110) plane. In this position the 'streamers' and the subsidiary spots are symmetrical about the horizontal line joining the direct spot and the Laue spot (Figs 2a, b, c, Plate XXX). Other settings of the crystal were tried for which the plane of incidence was inclined to the symmetry plane. The two 'streamers' and the two subsidiary spots accompanying the main dynamic reflection are found to be dissimilar in intensity and

unsymmetric with respect to the line joining the direct spot and the Laue spot. Even the primary Raman reflection lies outside this line in these cases; but this is clearly detectable only when the reflection is sufficiently away from the Laue spot and then the subsidiary phenomena become extremely weak.

The question whether the subsidiary phenomena separate from the primary quantum reflection as the glancing angle of incidence θ , is gradually decreased from the Bragg value θ_B was studied. It was found that the region of maximum intensity along the 'streamer' gradually shifted away from the strong Raman reflection, thereby showing that the streamer was a specular reflection very much elongated by the divergence of the beam and the obliquity of the corresponding phase vector to the surface of the sphere of reflection. However, whether there is a bridge connecting this region of maximum intensity to the main Raman reflection or not can be settled only by the use of very fine beams having the divergence of only a few minutes of arc.

3. Explanation of the Phenomena

The direction of the Raman reflection is found with the help of the 'sphere of reflection'. The direction of incidence is represented by $\vec{OI} = 1/\lambda$ and the vector \vec{IC} represents the reciprocal lattice vector $1/d$. When C is

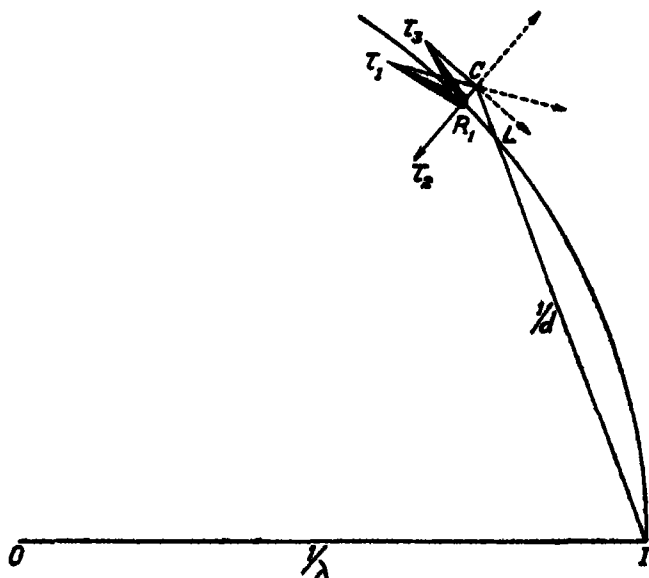


FIG. 1. Geometry of the Raman Reflections

on the sphere of reflection, the Bragg reflection is observed. No classical reflection is possible when C is either inside or outside the surface of the sphere of reflection. $C\tau_1$, $C\tau_2$ and $C\tau_3$ represent the directions of the reciprocal vectors of the phase wave-lengths of the lattice oscillations excited by

the incident X-rays, and respectively parallel to the three cube edges of the unit cell of diamond. These phase-waves combine with the static lattice spacings and give rise to dynamic stratifications which produce the Raman reflections whenever the reciprocal vectors of these resultant spacings fall on the surface of the sphere of reflection.

If the plane of incidence is a symmetry plane, $C\tau_2$ is in the plane of incidence and the Raman reflection lies in the same plane as the classical reflection. The quantum reflections caused by the two vectors $C\tau_1$ and $C\tau_3$ are symmetric with respect to this plane. When C is outside the sphere, i.e., $\theta < \theta_B$, $C\tau_1$ and $C\tau_3$ make only *small* angles with the surface of the sphere of reflection and they give rise to very elongated spots, which appear as 'streamers' due to the finite *divergence* of the beam (Fig 2a, Plate XXX). On the other hand when the end C of the reciprocal lattice vector is within the sphere of reflection, i.e., $\theta > \theta_B$, the vectors $C\tau_1$ and $C\tau_3$ meet the sphere at larger angles and give rise to two quantum reflections, which are drawn out into two elliptic spots (Fig 2c, Plate XXX) by the divergence of the beam.

In a previous paper² by one of us a quantitative formula was derived for the distance of the subsidiary spot from the main Raman reflection in terms of the distance between the Laue spot and the Raman reflection, for the symmetrical setting. It is approximately

$$0.68 \operatorname{cosec} (35^\circ 16' - \theta)$$

Actual measurements for two different settings of the crystal giving the subsidiary spots are given below —

Plate distance = 4.35 cms

Glancing angle of incidence	Distance between Laue spot and Raman spot	Distance between the primary Raman spot and a subsidiary spot	
		Experimental	Theoretical
22° 24'	1.2 mm	3.5 mm	3.7 mm
23° 28'	2.8 mm	7 mm	9.3 mm.

However, when the plane of incidence is not a symmetry plane, $C\tau_2$ is not in the plane of incidence and $C\tau_1$ and $C\tau_3$ are no longer symmetric with respect to the plane of the classical or Laue reflection. Hence in both the cases $\theta > \theta_B$ and $\theta < \theta_B$, the subsidiary spots and the 'streamers' are unsymmetrical, and the difference in the lengths of the reciprocal vectors $C\tau_1$ and $C\tau_3$ give different intensities for these reflections, as actually observed. Figs 2d, e and f in Plate XXX show the 'streamers' and the subsidiary spots when the plane of incidence makes 10° with the symmetry plane.

The inclination of the vectors $C\tau_1$ and $C\tau_3$ to the surface of the sphere being small (only about 13°), a rotation of the whole configuration through 10° with IC as axis would make one of these vectors leave the surface of the sphere. Hence, only one of the 'streamers' would be left behind and this would extend both ways if the setting is the correct Bragg setting.

The existence of these triple quantum reflections suggests that the three sets of phase-waves are not capable of combination among themselves, thus showing that the lattice oscillations are incoherent when they differ in phase-wave-lengths. Otherwise, we would have phase-waves of all possible orientations thus destroying the specular character of the quantum reflections. However, the quantum reflections are distinctly separate only when the crystal setting is off the Bragg setting by the divergence of the incident beam or more. The phase-wave-length corresponding to the quantum reflection in this position is nearly 150 \AA or less. For nearer settings, the operative phase-wave-lengths are much greater, but due to the divergence of the beam we are not in a position to settle whether the corresponding lattice oscillations are coherent or not.

The question of coherence or incoherence of the lattice oscillations of different phase-wave-lengths in the direction of the three cube-edges of diamond, was tested out experimentally in light scattering by Nayar.³ A crystal of diamond was illumined by a narrow parallel pencil of light incident at the correct angle so that the phase-waves parallel to a cube face may reflect the light with altered frequency. The scattered light was observed spectrographically in the proper direction of reflection and in directions up to 20° on either side of it. He found that the Raman line exhibited the same intensity in all these directions. The facts about light scattering indicate therefore, that lattice oscillations of phase wave-lengths of 2000 \AA or more are coherent and that they combine to give phase waves of all possible orientations. In the X-ray field this means a change in the glancing angle of only a few minutes of arc from the correct Bragg setting. Hence the problem of coherence in diamond of the lattice oscillations for different phase-wave-lengths can be settled only by observing the subsidiary phenomena with X-ray beams having a divergence of 5 minutes of arc or less.

4 *Remarks on the Influence of Mosaic Structure in Diamond*

The X-ray experiments and the spectroscopic investigations in this laboratory have all been conducted with the ordinary type of diamond. The theoretical investigations have also been carried out only for the perfect crystals. The studies of Julius, Angstrom and Reinkober⁴ have shown the existence of a second variety of diamond which, unlike the ordinary variety, is transparent to the infra-red radiations in the neighbourhood of 8μ .

Robertson, Fox and Martin⁵ have made extensive investigations on the various properties of this type of diamond and have come to the conclusion that it possesses a definite mosaic structure. A specimen of this type has been recently procured in this laboratory, but no X-ray studies have been conducted with it as yet. While this paper was going to press, a note in *Nature* by Lonsdale and Smith⁶ has reached India where it is stated that this rare type of diamond does not exhibit the subsidiary phenomena forming the subject of the present paper, and also indicating that the ordinary or Bragg X-ray reflections given by it are stronger. It is shown below that the mosaic structure readily explains these facts.

Robertson, Fox and Martin have remarked that the second type of diamond gives a higher value for the ratio of the intensity of the (111) reflection to that of the (222) reflection than the ordinary type and have put this forward as an evidence of its mosaic structure. In a paper⁷ appearing in this issue of the *Proceedings*, one of us has shown that the (222) reflections can be explained quantitatively as Raman reflections produced by the lattice oscillations of *infinite* phase-wave-length produced in the crystal. In a rotation or oscillation method, the (111) planes of a mosaic crystal would give the reflection over a greater angular range so that its intensity would be more than that for the normal type. On the other hand, the (222) quantum reflection would be much weaker as the size of the mosaic would effectively prevent the co-operation between the neighbouring parts of the crystal required for such a weak reflection to manifest itself. Hence it is not surprising that the ratio of the intensity of the (111) to the (222) reflection is large for the second type of diamond.

In another paper⁸ appearing in this issue, one of us has pointed out the great rapidity with which the intensity of the Raman reflection falls off with decrease in the phase-wave-length of the lattice oscillations. It means therefore, that even for a perfect crystal the structure amplitudes for these subsidiary reflections are extremely small, so that very large numbers of regular co-operating planes are needed to produce an appreciable intensity of the subsidiary reflections. In a mosaic crystal, the lack of co-operation between different mosaic blocks would therefore reduce the intensity of the subsidiary reflection to a small fraction of the value for the perfect crystal. Hence it is but natural that the subsidiary phenomena, weak even with a perfect crystal, cease to be observable with the rarer type of diamond whose mosaic structure is an accepted fact.

Lonsdale and Smith have also observed that the Raman reflections are absent, (a) along the (001) axis for the (220) and (113) dynamic planes, (b) along the (010) axis for the (202) and (131) planes, and (c) along the (100) axis for the (022) and (311) planes. This fits in beautifully with the concept

of phase wave-normals along the three cube edges, in which case the observed inactive directions are exactly tangential to the surface of the sphere of reflection when the plane of incidence is a symmetry plane. In this setting the other two phase vectors cut the sphere of reflection in the plane of incidence.

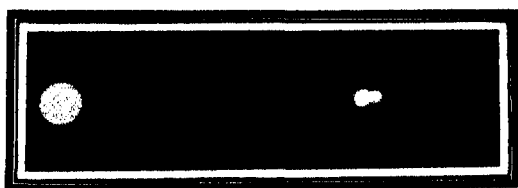
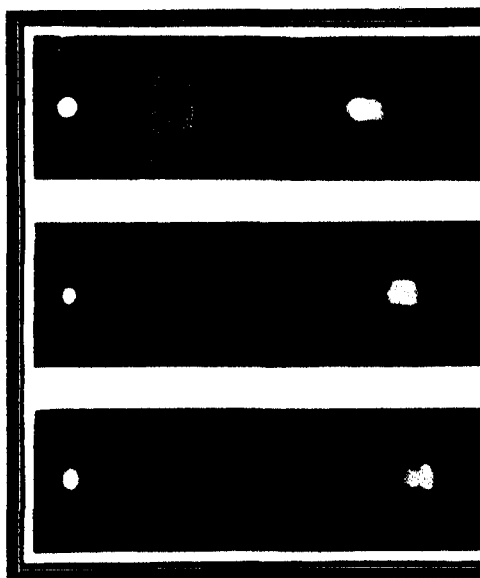
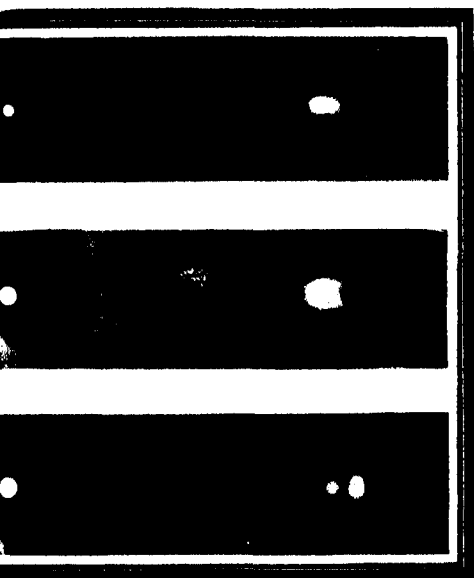
The authors wish to record their deep sense of gratitude to Sir C. V. Raman, Kt, F.R.S., for his kind and helpful guidance in the course of this work.

5 Summary

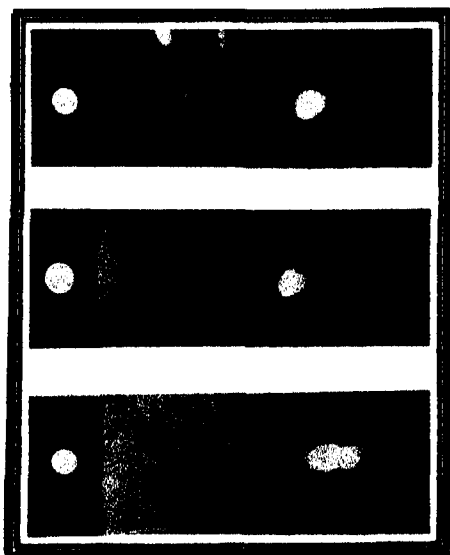
The existence of three sets of phase waves of the lattice oscillations in diamond is shown to give rise to three quantum or Raman reflections from the (111) planes. Two of these reflections form very elongated spots which appear as streamers, due to the divergence of the beam and the obliquity of the corresponding reciprocal phase vectors, when the glancing angle of incidence θ is smaller than the Bragg angle θ_B . These reflections appear as discrete subsidiary spots when $\theta > \theta_B$. The behaviour of these reflections with respect to intensity and orientation, when the plane of incidence of the classical reflection is (1) parallel to, and (2) inclined to, a (110) symmetry plane of the crystal, is described and accounted for. The question as to the coherence of the lattice oscillations of differing phase-wave-lengths has been examined, and it is shown that all oscillations of phase-wave-lengths of the order of a thousand lattice spacings or more are coherent, while those with phase-wave-lengths of the order of a hundred lattice spacings or less are definitely incoherent. But the exact stages at which the incoherence sets in is still unsettled. The differences in the behaviour of the various planes in the normal type of diamond towards the subsidiary spots and 'streamers' and the absence of the subsidiary phenomena in the rare type, both observed by Lonsdale and Smith, have been accounted for. The larger value of the ratio of the intensity of the (111) to the (222) reflection as recorded by Robertson, Fox and Martin for the type II diamond is explained on the basis of its mosaic structure.

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ON THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: IV. BENZIL

BY R. V. SUBRAHMANYAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

EARLY in the history of the study of X-ray diffraction in crystals following Laue's discovery of 1912, it was realised that the disturbing effect of the thermal agitation on the X-ray phenomena was a matter of considerable importance. About the same time, the theory of the specific heat of solids due to Debye in which the thermal energy of crystalline solids was identified with that of the elastic vibrations in them was coming into general favour. It was therefore natural that the considerations of the temperature effect in X-ray diffraction should be based on the same hypothesis. In fact, the first attempt in this direction was made by Debye himself, and the further improvements of the theory both by Debye and by later workers in the field rested on his basic concepts. Even in the specific heat theory of that time, however, it was recognised that the thermal energy of crystals which were not of the simplest chemical composition included what were called "Einstein" terms arising from modes of molecular vibration with specific frequencies. That these vibrations had any part to play in the X-ray phenomena does not however, appear to have been realised either by the experimenters or by the theorists. The great importance of the Einstein vibrations in X-ray physics, and the striking and distinctive phenomena to which they give rise, were first pointed out by Sir C. V. Raman and Dr P. Nilakantan in their article in *Current Science* for April 1940. The study of these phenomena, in fact, has opened up a new approach to the problems of the solid state. The importance of the Einstein or characteristic frequencies of the crystal lattice is particularly evident in considering the X-ray behaviour of organic crystals. Taking for instance the case of benzil, it is known (Allen, 1927 and Banerjee and Sinha, 1937), that the hexagonal lattice of this crystal contains 3 molecules per unit cell. Even ignoring the numerous possible "internal" modes of their vibration, we have still to consider no fewer than 18 degrees of freedom of molecular movement, of which no less than 15 are necessarily represented by specific frequencies of vibration; the remaining three degrees of freedom alone of translatory movements of the lattice cell are the maximum number which can possibly be assigned to "elastic

vibrations" of the Debye type. It is thus evident that, in organic crystals, the Einstein vibrations of the lattice involving hindered rotations or translations of the molecules are of far greater importance than any possible vibrations of the elastic solid type

In the three preceding papers of this series, Dr C S Venkateswaran has considered respectively the cases of naphthalene, benzophenone and hexamethylene-tetramine. His work has proved conclusively that the situation is as described in the preceding paragraph. In the two crystals of the aromatic class dealt with by him, the very striking result emerged that the lattice planes which are parallel or nearly parallel to the planes of the aromatic rings give Raman reflections of marked intensity, while those perpendicular or nearly perpendicular to them are, by comparison, practically inactive in this respect. In fact, a striking disproportion was evident in the relative intensities of the classical and quantum reflections by the crystal planes differently situated with respect to the planes of the aromatic rings. Dr Venkateswaran has remarked that these results find a simple explanation in the nature of the molecular oscillations which vary the structure amplitudes of the crystal planes. The hindered rotations and translations of the molecules as well as the deformational oscillations of low frequency would almost exclusively vary the structure amplitudes of the planes parallel to the aromatic rings, leaving unaffected those nearly perpendicular to them.

The fact that benzil is very similar in chemical composition to benzophenone, the former being diphenyldiketone and the latter diphenylketone, made it desirable to include this substance in the present series of investigations. It may be mentioned in this connection that a few photographs obtained with benzil were reproduced with a note in *Nature* (1940) published by four workers of the Royal Institution in London.

2 Crystal Structure of Benzil

Benzil belongs to the same crystal type as α -quartz, and has, in fact, an optical rotatory power stronger than that of quartz along the hexagonal axis. As already mentioned, the unit cell contains three molecules. The dimensions of the cell are $a_0 = 8.15$ A.U. and $c_0 = 13.46$ A.U. and the X-ray evidence indicates that the three molecules are arranged in equivalent positions within the cell about the threefold screw axis. Krishnan, Guha and Banerjee have studied the diamagnetic behaviour of the crystal and found that the gram-molecular susceptibility along the trigonal axis is $\chi^a = -80.0 \times 10^6$ e.m. units and that perpendicular to the trigonal axis is $\chi_\perp = -125.6 \times 10^6$ e.m. units. The crystal shows a noticeable birefringence, $\omega = 1.6588$, and $\epsilon = 1.6783$ (Groth, *Chemische Kristallographie*) for the sodium line. Suggestions regarding the molecular structure and the molecular

orientation in benzil were made by Banerjee and Sinha (*loc cit.*), but these conclusions have been disputed by Lonsdale and Knaggs (1939) in a brief note. No definite conclusions regarding the structure of benzil appear, however, to have been published by these latter authors.

3 *Experimental Arrangements*

Benzil is usually crystallised from ether. Due to the rapid evaporation of ether, most of the crystals are often found to be of disproportionate growth, forming a cluster. In the present work, the crystals were grown out of a solution of the substance in alcohol diluted with an equal volume of water. The smaller solubility of the substance in alcohol, assisted by the slow evaporation of the liquid facilitates a good growth of crystals suitable for X-ray work. The crystals were yellow hexagonal prismatic needles, approximately $\frac{1}{2}$ mm in diameter. The source of X-rays was a Siefert 'Spektro-Analyt' tube of the non-demountable type, with a copper anticathode, run at 41000 volts, and 10 m a. A fine beam of X-rays collimated by means of a lead slit 1 mm in diameter and 9 cm deep was incident on the crystal which was mounted on a goniometer with its trigonal axis nearly vertical. Initially one of the external prism planes of the crystal was normal to the X-ray beam, this having been judged by the optical reflection from that face. The crystal was turned through an angle of about 20° from this position about the vertical axis of the goniometer, which was adjusted to coincide with the triad axis of the crystal. The plane giving an intense Raman reflection along the horizontal was found to be the $2\bar{2}00$ plane, and a series of pictures was then taken up to a limit of about 4° on either side of this setting. In these extreme positions, exposures varying from about 2 to $2\frac{1}{2}$ hours were required.

For another series of pictures, the crystal was mounted in such a way that the X-ray beam passed along the trigonal axis. By suitable manipulation of the crystal this way or that about the goniometer axis, and aided by a number of trial pictures, the exact direction of the beam along the trigonal axis was secured. In this position, exposures varying from 2 to 3 hours were found necessary to secure a well-exposed pattern.

4. *Description of the Experimental Results*

Only two of the typical photographs obtained have been reproduced, although a number of others in different settings of the crystal have been taken. Fig 1 *a* in Plate XXXI represents a symmetric Laue photograph with the X-rays passing along the trigonal axis of the crystal, while Fig 1 *b* represents one with the X-rays perpendicular to the trigonal axis. Both photographs reveal some very interesting features. It will be observed from Fig 1 *a*, that the Laue pattern exhibits hexagonal symmetry with respect to the positions of the spots. The *intensities*, however, exhibit only a trigonal

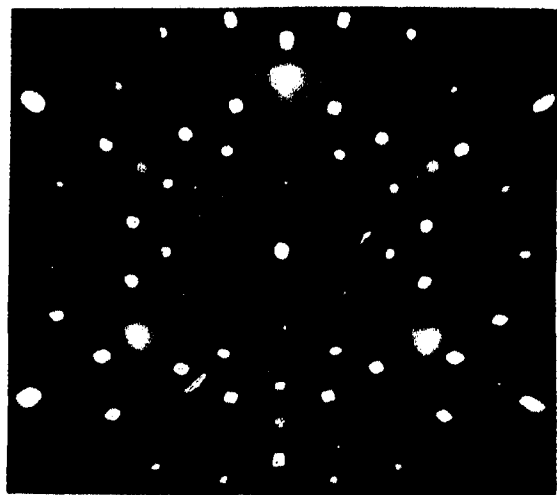
symmetry, alternate sectors showing noticeable differences in the intensity of the spots. This feature is particularly striking in the Raman pattern of six spots at the corners of a regular hexagon; the alternate spots are of the same intensity, but differ greatly from the intervening ones in this respect. Though no quantitative measurements of intensity have been made, it is fairly clear that these differences are much greater than those of the corresponding Laue spots forming a hexagonal pattern. It is also noticed that streamers emerge from the primary Raman spot, proceeding approximately parallel to the adjacent sides of the hexagon, a noteworthy feature being that these alternately point in opposite directions. The three pairs of spots showing the intense Raman reflections have been identified as belonging to the form $(2\bar{2}01)$. Lying on the same radial lines as these and forming an outer hexagon are the spots of the form $(3\bar{3}02)$ which have however much less intensity. In two of them the Raman K_α spots are just visible beyond the Laue position, two of the other spots of this group coinciding with the Bragg reflection. Here again in the neighbouring Raman spots, the intensities appear to differ.

Equally remarkable are the features seen in Fig. 1 *b*, obtained as has already been mentioned with the direction of the X-ray beam normal to the trigonal axis of the crystal. There are two groups of Laue spots lying along two ellipses. These are accompanied by two groups of Raman spots lying on vertical lines in the photograph. The group to the left of the picture is much more intense than the group to the right, while in each group, the spots differ notably in intensity among themselves, the order of relative intensities is exactly reversed on the two sides of the picture. The zone to which the more intense Raman spots belong has been identified to be the (110) zone, while the other is the $(1\bar{1}0)$ zone. On the left, the central Raman spot lying along the horizontal has the index $2\bar{2}00$, the one immediately above and below belong to the $2\bar{2}01$ planes, and the one further up that of the $2\bar{2}02$ plane. On the other zone the corresponding spots which appear belong respectively to the $\bar{2}110$, $-\bar{2}111$ and $-\bar{2}112$ planes. Of all the Raman spots seen, by far the most intense is that given by the $2\bar{2}01$ plane. It is thus exactly the same set of planes which give the intense reflections seen in Fig. 1 *a*.

5. Discussion of the Results

Bearing in mind what has been said already in the introduction, it is clear that the only possible explanation for the results indicated is that the plane of the aromatic rings in the benzil crystal lie in or very close to the alternate planes of the form $(2\bar{2}01)$. It is readily seen that this explains every one of the features indicated above. The angle between the triad axis of the crystal and the $(2\bar{2}01)$ plane is by calculation $14^\circ 6'$. It is thus evident that the plane of the aromatic rings in the crystal are inclined to the triad axis at an

(a)



(b)

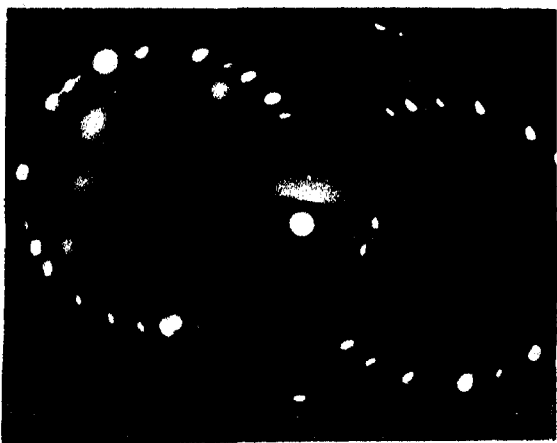


FIG. 1

Raman X-ray Reflections in Benzil

angle about the same as that stated above. The inclination of the plane of the aromatic rings thus directly inferred from the X-ray photographs, agrees closely with the angle 13° calculated by Banerjee and Sinha from the magnetic measurements of Krishnan, Guha and Banerjee. It should be remembered that the X-ray method is definitely superior to the magnetic method as it indicates both the azimuth and the orientation of the planes and not merely the latter.

The explanation of the configuration of the streamers accompanying the Raman reflections is fairly simple. By symmetry, the phase waves of the lattice must be along the three planes inclined at 120° to each other and passing through the triad axis of the crystal, these planes being perpendicular to the longer axis of the benzil molecules. The directions of the streamers as observed conform to this situation.

My sincere thanks are due to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his invaluable help and inspiring guidance throughout the course of this investigation.

6 Summary

In a series of well-exposed Laue diagrams of benzil taken with a pencil of Cu X-radiation along the trigonal axis, three alternate planes of the form $(2\bar{2}01)$ are found to give intense Raman reflections, the alternate planes of the same form being much less active in this respect. A similar feature is also observed in photographs taken with the beam transverse to the trigonal axis. The facts find a very simple explanation when it is assumed that the three molecules of benzil in the unit cell lying in equivalent positions along the threefold screw axis, have the planes of their aromatic rings practically coinciding with the planes mentioned. The inclination of 14° of the aromatic planes thus inferred from the X-ray results is in close agreement with the angle of 13° deduced from the diamagnetic susceptibilities of the crystal. The X-ray method is however obviously superior as it gives both the azimuth and orientation of the aromatic rings.

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QUANTUM REFLECTION OF X-RAYS IN CALCITE

BY P NILAKANTAN AND P G N NAYAR

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. Introduction

CALCITE is usually regarded as a crystal suitable for precision X-ray research, the intensity of the reflections given by it being much nearer those calculated for an ideal crystal than for instance in the case of rock-salt. Calcite should therefore be particularly well-suited for quantitative studies of the type of X-ray reflection which involves a change of frequency and is analogous to the well-known Raman effect in crystals. A strongly exposed Laue photograph showing numerous such reflections by the crystal planes of calcite was reproduced with a letter by Sir C V Raman and Dr P Nilakantan under date the 18th of August 1940 which was published in the issue of *Nature* dated the 19th October 1940. Attention was there drawn to the appearance in the photograph simultaneously of the quantum reflections of the first, second and third orders by the cleavage planes of calcite, as well as the well-defined character of the quantum reflections. In the present paper, some further observations on the subject are described and additional photographs are reproduced.

The explanation of the appearance of X-ray reflections with altered frequency is, broadly, that the encounter between the X-ray quantum and the crystal lattice results in the infra-red vibrations of the latter being excited, the incident quantum going off with diminished energy in a direction determined by one or other of the different sets of lattice planes in the crystal. The possibility of such a process and the experimental evidence that it actually occurs in the case of the (111) planes of diamond was indicated by Sir C V Raman and Dr P Nilakantan in an article in *Current Science* for April 1940. In view of the universality of the phenomenon and its great significance in crystal physics, it would appear desirable to present some considerations of an elementary character which may help to elucidate these new ideas.

Regarding a crystal as a pattern in space of atoms, molecules or ions grouped together in an orderly fashion, we notice that the essential feature of it is the repetitive or periodic character of such arrangement. It is this periodicity which gives us the regularly spaced layers of atoms capable of giving monochromatic X-ray reflections of the usual kind when the rays are

incident on them at an appropriate angle. The concept of a crystal as a purely static ordering of atoms is, however, untenable since such static arrangement can be disturbed in a variety of ways, in particular, by the incidence of the radiation itself, as actually happens in the Raman effect with visible light. It is necessary, in fact, to consider the various possible modes of vibration of the regular assemblage of atoms which we call a crystal. For such a vibration to possess a frequency which can be specified with perfect mathematical rigour, the disturbance should be completely periodic both in space and time, in other words, the ions, atoms or molecules should vibrate in identically the same way, with the same frequency, amplitude and phase in all the lattice cells of the crystal. During such a vibration, the crystal does not lose its character as a space-periodic grouping of the atoms, but becomes in addition a time-periodic structure. It is vibrations of this type which are characteristic of the crystalline state and which appear as sharply-defined lines in the Raman spectra.

Applying now the same electrodynamic principles as those by which Laue derived his well-known conditions for the observation of X-ray diffraction in crystals, we see that the secondary radiations from the atoms in a crystal executing monochromatic vibrations automatically divide themselves into three groups, those of the original or undisturbed primary X-ray frequency ν and two others having frequencies $\nu \pm \nu^*$, where ν^* is the frequency of the atomic vibration. Since ν^* is a strictly monochromatic frequency, the radiations from the atoms in the different lattice cells having a frequency $\nu + \nu^*$ or $\nu - \nu^*$ should be capable of interfering with each other and therefore also of giving diffraction patterns having these radiation frequencies in the same way as the radiations of unmodified frequency ν . The situation, it will be noticed, is closely analogous to that arising in the Raman effect. It should be emphasised that such X-ray reflections with altered frequency are possible only when the atoms in all the lattice cells vibrate in identically the same fashion, in other words, with vibrations having the characteristic crystal frequencies. The position is entirely different in regard to the ordinary or elastic vibrations of the lattice. These have a continuous spectrum of frequencies and merely disturb the regularity of the crystal structure. They give rise to a weak X-ray scattering which should be unobservable except when relatively large volumes of the crystal are operative. The introduction of quantum-theoretical ideas in dealing with either type of effect becomes inevitable in view of the change of frequency, exactly as in the case of the Raman effect. The alteration of frequency means an exchange of energy between the X-ray quantum and the crystal, and this can only occur in one direction or in the other, but not in both directions simultaneously. Accordingly,

we would in general have at low temperatures *only* the reflections of diminished frequency, $\nu - \nu^*$, reflections of increased frequency $\nu + \nu^*$ being however possible at higher temperatures.

2 *Crystal Structure and Lattice Spectrum of Calcite*

As is well known, calcite crystallises in the rhombohedral division of the hexagonal system. The distribution of the Ca and CO_3 ions around each other as indicated by the X-ray analysis is very similar to that of the Na and Cl ions in the rock-salt lattice. The calcite lattice may, in fact, be described as a distorted rock-salt structure, the distortion arising from the fact that the oblate CO_3 group replaces the spherically symmetrical Cl ion in it. The Ca and CO_3 ions lie alternately along lines parallel to the trigonal axis of the crystal.

The various modes of vibration with specific frequencies of which the calcite structure is capable may be divided into three groups. (a) internal vibrations of the CO_3 groups, (b) rotational oscillations of the CO_3 groups about axes respectively parallel and perpendicular to the trigonal axis and (c) translatory vibrations of the Ca and CO_3 ions relative to each other. So far as the X-ray problem is concerned, vibrations of the class (a) may be left out of consideration in view of their high frequency and relatively small effect on the structure amplitudes of the crystal planes. We are therefore principally concerned with vibrations of the classes (b) and (c). Here again, except with reference to certain special planes in the crystal, it may be assumed that the vibrations of the class (c), namely, movements of the Ca and CO_3 ions relative to each other are the more important, as they would influence the structure amplitudes of the lattice planes strongly. Such vibrations may be divided into two sub-classes, namely, those in which the movements of the Ca and CO_3 groups are predominately parallel to the trigonal axis, and those in which the movements are perpendicular to it. Vibrations of the first sub-class would influence the lattice planes normal or nearly normal to the trigonal axis, while those of the second sub-class would leave these unaffected. The position would be reversed with regard to crystal planes which are nearly parallel to the trigonal axis.

Raman effect investigations show that calcite has two low-frequency vibrations having wave-number shifts of 156 and 283 respectively. The latter is almost certainly a rotational oscillation of the CO_3 group about a line perpendicular to the triad axis. In the long-wave region of the infra-red spectrum, Liebisch and Rubens observed reflection maxima at 106, 330 and 357 wave-numbers, the second of these appearing only in the ordinary ray. It must be assumed that there are in addition, other modes of vibration which are inactive both in infra-red absorption or reflection and in the Raman effect.

The existing theoretical investigations of the vibrations of the calcite lattice concern themselves with the unit-cell containing two Ca CO_3 groups. It is not yet clear whether these give a really satisfactory explanation of the observed spectroscopic behaviour of calcite.

3 Specular Character of Raman Reflections

Figs 1*a* and *b* in Plate XXXII reproduce two X-ray diffraction photographs obtained using copper K_α radiations and a needle-shaped crystal of calcite bathed by the X-ray pencil. The needle was prepared by dissolving out a cleaved rod of calcite in dilute hydrochloric acid until it was thin enough, thus avoiding all possibility of spurious effects due to distortion of the crystal or formation of disturbed surface layers. The needle is seen as a dark shadow crossing the direct X-ray beam. The Laue and the Raman reflections by the (211) planes of the crystal are seen side by side, the former in two different positions corresponding to the two different settings of the crystal, while the latter appears in the two pictures as a narrow streak in directions making nearly the same angle in both cases ($14^\circ 44'$ and $14^\circ 47'$) with the direction of the incident rays. The dynamic spacing calculated from these angles is practically identical with the known static spacing of the (211) planes of calcite, namely 3.03 Å.

Figs 3*a*, *b*, *c* and *d* in Plate XXXIII reproduce a series of four Laue photographs obtained with a thin and perfectly flawless cleavage plate of calcite. The X-rays from a molybdenum target tube run at 45000 peak voltage and 12 milliamperes were employed, the beam emerging from a cylindrical pin-hole 93 millimetres deep and 1.6 millimetres diameter. The plate to film distance was 5 centimetres. In Fig 3*c*, the X-ray beam was nearly normal to the cleavage face of the crystal, while in Figs 3*b* and 3*d*, the beam made angles of $7^\circ 14'$ and $5^\circ 16'$ respectively with the normal to the surface. In Fig 3*a*, the X-ray beam grazed a set of lattice planes within the crystal parallel to an external surface of cleavage. The photographs being well-exposed, they exhibit, besides the usual Laue reflections a great number of quantum reflections by the lattice planes of the crystal which may be readily identified from the angular positions of the spots with reference to the direct X-ray beam.

Though the Raman reflections as recorded in the photographs do not appear so sharply defined as the Laue spots, it should not be supposed that this is due primarily to any inherent diffuseness in the reflections. This is clearly indicated by Figs 1*a* and *b* where their linear width as recorded on the plates appears actually less than that of the more strongly exposed Laue reflections. As explained by Mr. Rama Pisharoty in the July 1941 issue of

these *Proceedings*, very striking differences in the appearance of the Laue and the Raman reflections arise as the result of several factors, namely (a) the finite lateral extension of the X-ray beam, its angular divergence and the variation of its intensity within the cross-section of the beam, (b) the difference in the nature of the reflection, *viz.*, white and monochromatic respectively, as also the difference in their relative intensities and the geometric laws which they obey, and (c) the finite thickness of the crystal employed. The X-ray beam employed in obtaining Laue photographs has usually a considerable angular divergence, being in the present experiments nearly 2 degrees of angle. Fig 4 in the text illustrates the effect of the arrangement employed to restrict the divergence of the beam on the distribution of intensity inside it

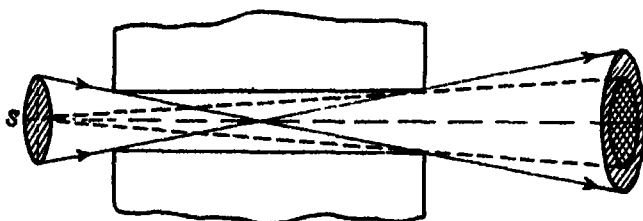


FIG 4 Cross-Section of X-Ray Beam

It is evident from the figure that there would be an intense central part in the emerging beam having a diameter slightly larger than that of the pin-hole and a less intense peripheral part, these we may designate as the umbra and penumbra respectively. The reflection of the intense central cone of rays would naturally be the first to be recorded, while the reflection of the penumbral rays would follow later. Accordingly, unless the exposures are sufficiently prolonged, a certain lack of sharpness in the boundary of the reflection is inevitable. A similar lack of definition at the edges would also result from the finite thickness of the plate, as illustrated in Fig 5. This again would be much more obvious in recording a weak reflection photographically than a strong one.

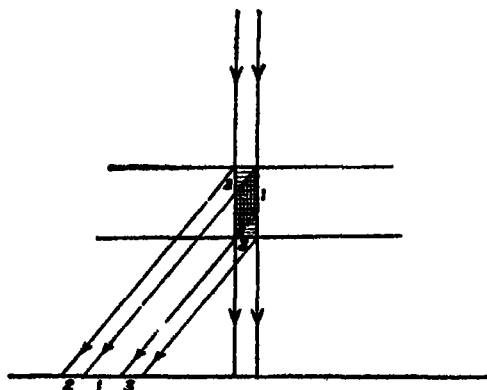


FIG. 5. Reflection from a Plate of Finite Thickness

4 Geometry and Intensity of Raman Reflections

FIG. 6. Raman Reflections in Calcite Crystal

Comparing Fig 3 *c* with Figs 3 *b* and 3 *d*, it will be seen that though the Laue patterns themselves are completely different, the Raman reflection patterns show only changes of intensity and no noticeable changes in the position of the spots

Table I gives a detailed list of all the crystal spacings in calcite which have been identified from the Laue photographs as giving quantum reflections. The table has been put in to emphasise the fact that numerous crystal planes give these reflections and that within the rather restricted range of

TABLE I
Raman Reflections in Calcite

Miller Indices	Glancing angle θ	Glancing angle ϕ	Dynamic spacing in A.U.	Static spacing in A.U.	Intensity estimate
112	3° 2'	10° 18'	2.99	3.03	10
	9° 52'	3° 27'	3.04	3.03	10
	14° 39'	-1° 14'	3.06	3.03	3
224	9° 52'	19° 8'	1.52	1.52	2
	14° 39'	12° 11'	1.53	1.52	6
336	18° 50'	12° 28'	1.01	1.01	4
	19° 25'	11° 53'	1.01	1.01	
200	12° 19'	6° 53'	2.12	2.09	5
	13° 3'	6° 9'	2.12		5
	7° 8'	12° 8'	2.12		5
	6° 16'	13° 7'	2.11		4
400	18° 59'	20° 36'	1.05	1.045	6
	17° 29'	21° 52'	1.05		4
012	10° 27'	7° 24'	2.29	2.28	2
	10° 14'	6° 24'	2.32		2
	11° 23'	6° 45'	2.25		0.5
	10° 58'	7° 2'	2.27		
024	16° 26'	19° 20'	1.15	1.14	4
	16° 13'	19° 57'	1.14		4
	17° 54'	18° 30'	1.14		5
	17° 50'	18° 26'	1.14		5
T12	14° 54'	10° 18'	1.62	1.60	2
	13° 58'	11° 8'	1.63	1.60	3
	15° 17'	9° 43'	1.64		2
	15° 11'	10° 1'	1.62		2
	14° 40'	10° 38'	1.62		2
	15° 34'	9° 26'	1.64		2
323	12° 49'	8° 41'	1.90	1.91	10
	19° 3'	.	1.94		4
202	12° 37'	8° 41'	1.92	1.93	4
	17° 53'	.	1.97	..	.

TABLE I (contd)

Miller Indices	Glancing angle θ	Glancing angle ϕ	Dynamic spacing in A U	Static spacing in A U	Intensity estimate
235	19° 34' 19° 1'	15° 38' 16° 5'	1 17 1 17	1 18	3
556	20° 40' 20° 50'	19° 38' 19° 48'	1 02 1 02	1 03	6
512	16° 59' 17° 29'	22° 43' 22° 7'	1 04 1 04	1 04	2
411	22° 54' 23° 13'	20° 24' 20° 9'	0 96 0 96	0 96	1
446	20° 57' 21° 26'	18° 31' 17° 58'	1 05 1 05	1 06	2
435	18° 17' 18° 21'	15° 25' 15° 17'	1 23 1 23	1 23	4
302	12° 15' 12° 0'	15° 11' 15° 32'	1 50 1 49	1 47	1
301	13° 58' 14° 4'	12° 54' 12° 42'	1 53 1 53	1 52	5 4

settings of the crystal employed, the dynamic spacings do not diverge noticeably from the static values. Only in a few cases, however, are the settings sufficiently varied to enable any conclusions to be drawn about the value of the phase-wave inclination, θ , to the crystal planes under study. In the case of the (112) planes, for instance, there is a distinct progressive change of the dynamic spacing with alteration of the crystal setting, indicating that θ is definitely smaller than 90°. A more detailed investigation, however, would be necessary to settle this matter definitely.

A careful study of the Laue patterns shows that the Raman reflections do not always lie on the same radial line as the corresponding Laue reflections. A distinct lateral shift or azimuth effect is detectable in a number of cases. The streaks due to the white radiations are also in certain cases not radial. Only when the plane of incidence coincides with a crystallographic plane of symmetry that it can be definitely said that there is no lateral shift or azimuth effect. Usually, however, the Laue and Raman reflections are too near each other and the size of the spots too large to arrive at any definite conclusions. The fact that the azimuth effect is observable at least in certain cases indicates that the phase waves in calcite, as in diamond, have an orientation and an azimuth standing in definite relation to the crystal structure.

It may also be mentioned in passing that a careful analysis of the four Laue patterns reproduced as Fig. 3 revealed the presence of a few diffuse spots in each case whose origin could not be definitely identified.

The intensities shown in the last column of Table 1 are of course, only relative, and vary with the setting. They are, however, of some interest in relation to the question as to the relative intensity of the Bragg and Raman reflections by the individual planes. Theory indicates that there is not necessarily a proportionality between the static and dynamic structure amplitudes of a set of lattice planes, the latter depending on the particular modes of vibration responsible for the dynamic reflection. While broadly it may be said that the planes which give strong Bragg reflections, *e.g.*, the cleavage planes, also give strong Raman reflections, there are evidently exceptions to this rule. In particular, the (556) planes which are nearly normal to the trigonal axis of calcite give Raman reflections which are remarkably strong considering their relatively small static structure amplitude. It should be remarked in this connection that several of the possible lattice vibrations in calcite involve movements of the Ca and CO_3 ions along the trigonal axis, and hence should give marked variations of the structure amplitudes of planes normal to it. A fuller study of this point would obviously be of great interest.

Figs 2*a* and *b* in Plate XXXII illustrate the effect of rising temperature on the relative intensity of the classical and quantum reflections in calcite. The two types of reflection exhibit a reciprocity of behaviour, a marked diminution of intensity in the classical reflection with rise of temperature being accompanied by a marked increase of intensity of the quantum reflections. It is noteworthy that the (210) planes of calcite do not exhibit the exceptional behaviour observed with the same planes in sodium nitrate crystals.

5 Summary

The paper presents the results of a preliminary study of the X-ray reflections of the second kind observed in calcite. Numerous planes in this crystal exhibit such reflections, the dynamic spacings in most cases varying but little with the setting of the crystal. Observations are recorded concerning the sharpness of the reflections, their intensity and the influence of temperature on the same. The results are considered in the light of the quantum theory of X-ray reflection.

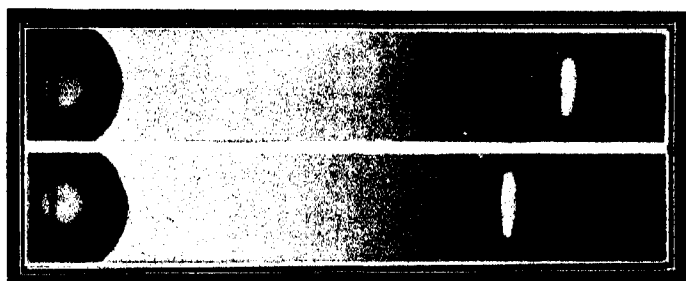
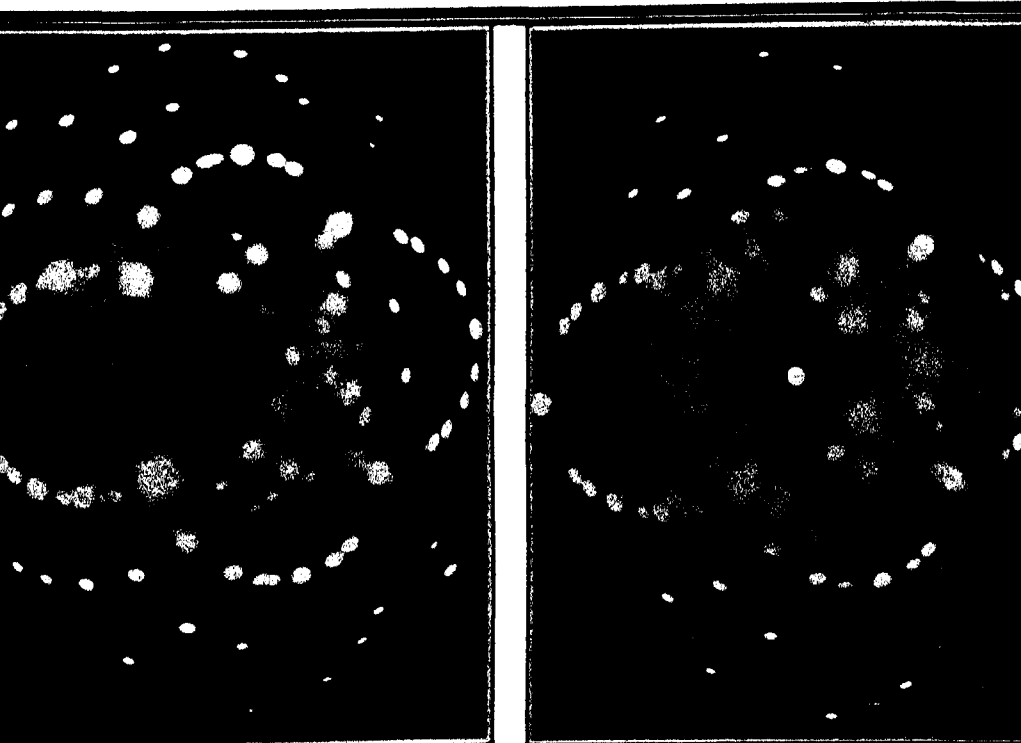


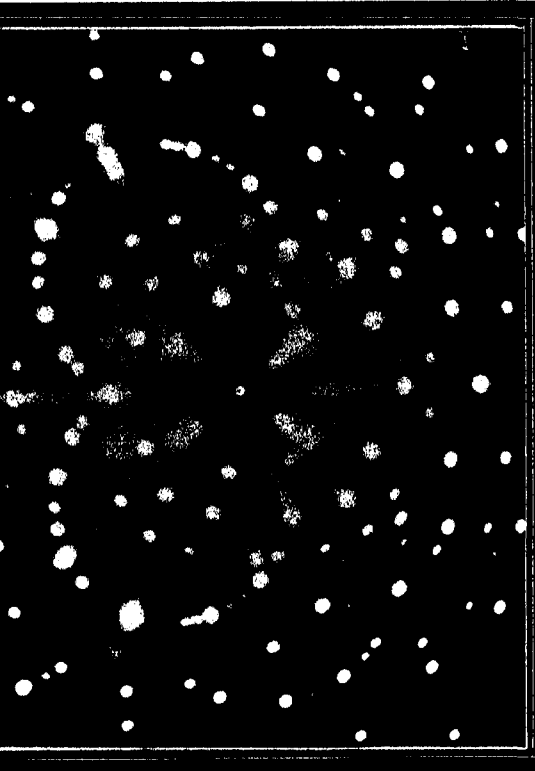
FIG. 1



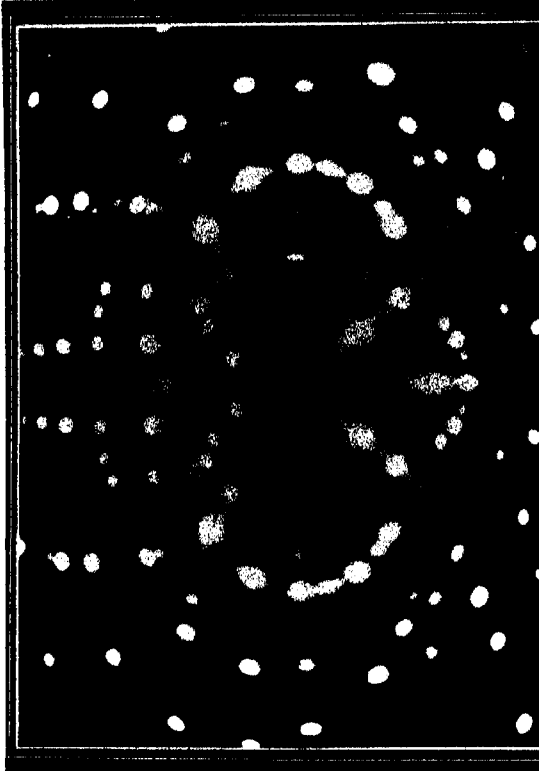
(a)
25° C.

FIG. 2

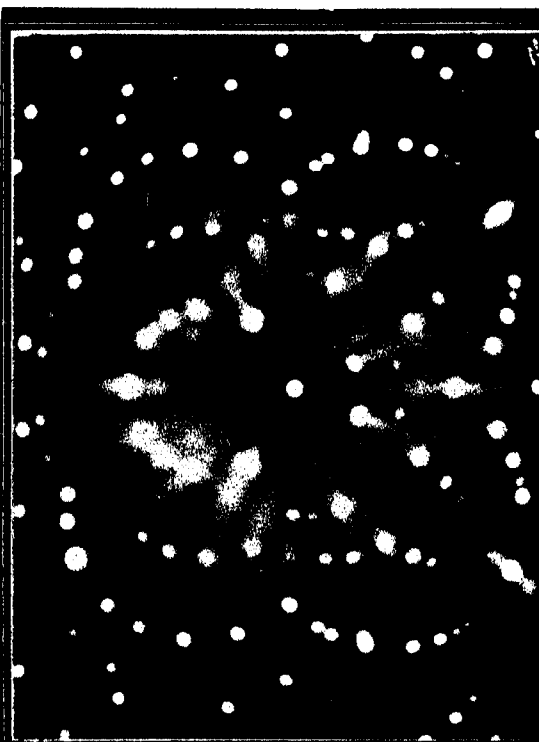
(b)
425° C.



(a)



(b)



THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: BASIC THEORY

BY SIR C V RAMAN, K_T, F R S, N L

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE first great step towards the development of a satisfactory theory of the specific heats of solids was taken by Einstein in 1907 when he showed that the acceptance of the hypothesis of radiation quanta involves as a necessary consequence that the mechanical energy of the vibrations of the atoms in a solid must also be regarded as consisting of discrete units or quanta proportional to the frequency of vibration. A quantitative relationship between the heat content of a solid and the "frequency spectrum" of its internal vibrations was thus indicated. The evaluation of the thermal energy of a solid accordingly depends on a determination of its vibration spectrum, in other words, a knowledge of the frequencies of atomic vibration and of the manner in which the available degrees of freedom are distributed amongst them. This is a problem of some difficulty to the solution of which there are two distinct methods of approach. The first is the phenomenological one, namely that of obtaining the desired information in some independent fashion, *e g*, by spectroscopic research. The other is the *a priori* method of finding the possible modes of vibration from a knowledge of the crystal structure and the forces acting between the atoms by a dynamical investigation. To the genius of Einstein we owe the first indication of both of these methods of approach to the specific heat problem. The reconciliation of the results obtained by the two methods with each other and with the specific heat determinations over a wide range of temperatures is obviously of the highest importance for a proper understanding of the physics of the solid state.

2 Nature of the Thermal Agitation in Crystals

A crystal is a periodic three-dimensional grouping in space of an immense number of atoms, ions or molecules held to each other by the interatomic or intermolecular forces. The structure being on an exceedingly small scale, the number of cells of the crystal lattice included in any volume of macroscopic dimensions is enormously large. This fact makes it possible to divide the possible modes of thermal agitation in a crystal sharply into two classes. *The vibrations of the first class* are on a relatively large scale and may be described without any reference to the fine structure of the solid. These are

the elastic vibrations of the crystal, their modes and frequencies are determined by the velocity of propagation of the elastic waves in it and the shape and dimensions of the external boundary of the solid. *The vibrations of the second class* are essentially dependent on the fine structure of the crystal. In view of the tremendous disparity in size between the lattice cells and the macroscopic dimensions of the solid, the shape and dimensions of the crystal are without influence on vibrations of this kind. They may be visualized and described as time-periodic variations from the static crystal structure. The vibrations of the first class involve oscillatory movements of large groups of atoms, while those of the second involve displacements in the relative positions of neighbouring atoms. The frequencies of vibration of the second class would therefore be much greater than those of the first. The dividing line between the two classes of vibration is most appropriately drawn at a frequency for which the wave-lengths of the elastic vibration are just large enough to justify the fine structure of the crystal being ignored.

The division here made of the possible modes of vibration of the crystal into two classes corresponds also to a fundamental difference in the character of the vibration spectrum in the two regions of frequency. Considering the elastic vibrations, it is evident that the larger the crystal, the smaller would be the frequency differences between the successive possible modes of vibration. Hence, *the elastic vibrations of a crystal of macroscopic dimensions give a continuous spectrum of frequencies*. The position is completely different in respect of the second class of vibrations. Here, as already remarked, the size of the crystal is not a relevant factor. As the vibrations involve periodic variations in the crystal structure, they may be pictured as forming dynamic repetition patterns in space related to the crystal structure in some simple way. The principal modes of vibration would be those in which the atomic movements occur in identically the same fashion in every lattice cell of the crystal. Less important, but nevertheless requiring consideration are periodic movements of a more general kind, *viz.* oscillations which have identically the same form in the cells of a superlattice which is a repetition on a larger scale of the static crystal structure, the spacings being an integral multiple thereof. All such vibrations would have uniquely defined frequencies, in other words, they would be monochromatic, and if the cells of the superlattice are not too large, they would also be finite in number. *The vibrations of the second class would thus appear as a set of discrete and enumerable monochromatic frequencies in the infra-red region of the spectrum.*

The manner in which the thermal energy of the crystal would be distributed amongst the various possible modes of vibration can now be readily visualized. The largest part of the thermal energy would be carried by the

modes of vibration which have been referred to as the principal lattice frequencies. These are obtained by considering a lattice cell having all the symmetry elements present in the crystal and thus fully representative of it. By applying the appropriate geometric and analytical methods, we find the number, character and frequencies of the various modes of vibration of the p atoms located in the cell. Such an analysis would yield $(3p - 3)$ modes of internal vibration and 3 translations for the cell as a whole. If p be fairly large, as is the case with the vast majority of crystals, the $(3p - 3)$ degrees of freedom appearing as vibrations would greatly exceed in number the 3 degrees of translation. The next stage in the analysis would be to consider a super-lattice of which the cells have twice the edge length of the lattice cells first chosen. Applying similar methods to it, we would have $(24p - 3)$ modes of internal vibration of the atoms included in the cell and 3 translations. The former would naturally include the $(3p - 3)$ modes of vibrations already considered, besides others approaching them in character, and we would obtain also new modes of vibration previously reckoned as simple translations of the unit cell. We may, if necessary, similarly proceed to consider a cell thrice as large which would give us $(81p - 3)$ modes of internal vibration and 3 translations, or even a cell four times as large which would give us $(192p - 3)$ internal vibrations and 3 translations. These refinements should, however, be unnecessary except for crystals in which p is a small number and usually not even in their case. Thus, when the analysis is carried sufficiently far, all the modes of vibration which make any sensible contribution to the thermal energy of the crystal may be identified, and the residue associated with the energy of the elastic vibrations of undefined frequency may be ignored. The number of the vibrations of the latter kind bears to the total number of degrees of atomic freedom a ratio of the same order of magnitude as the ratio of the volume of an individual atom to the cube of the limiting wave-length. When, therefore, the wave-length limit is even moderately large in relation to the lattice spacings of the crystal, the energy of such vibrations is a negligible fraction of the whole.

The results of our discussion may be summed up as follows: *In evaluating the thermal energy of a crystalline solid, we are only concerned with the discrete or monochromatic frequencies appearing in its infra-red spectrum which owe their origin to the displacements of the atoms from their positions of equilibrium in the characteristic structure of the crystal; the elastic vibrations which involve only a general distortion of the lattice may be left out of account altogether.*

3 The Specific Heat Theory of Debye

The result stated above is in direct contradiction with the assumptions made in the theory of specific heats of solids due to Debye. The latter

identifies the thermal energy of the crystal *ab initio* with that of the elastic vibrations. A property connected in the closest manner with the atomic or molecular structure of the solid is thereby sought to be interpreted in terms of purely molar concepts, namely density, elasticity and sound velocities, thus reversing the usual idea of a physical explanation. No theoretical or experimental justification can, however, be found for the basic assumption made in the Debye theory that the vibrations carrying the thermal energy are of the elastic solid type. The fact that elastic vibrations travel with a high velocity, while heat energy does not travel at all but only diffuses with extreme slowness, is sufficient in itself to make such an identification questionable. That the extrapolation, made in the Debye theory, of ideas derived from the physics of continuous media to the physics of atomic structures is not justifiable is indicated by the simple mechanical analogy of a periodically loaded string. Consider a string of finite length under tension T to which m loads, each of mass μ are attached at regular intervals a apart. The displacement of the r th load in the s th mode of vibration is given by the formula —

$$\psi_r = P_s \sin \frac{(r-1)\pi}{m+1} \cos(n_s t - \epsilon_s) \quad (1)$$

where

$$n_s = 2 \sqrt{\frac{T}{\mu a}} \sin \frac{s\pi}{2(m+1)} \quad (2)$$

Provided the integer s appearing in these formulæ is small compared with m , the vibrations approximate in form to those of a uniform string. As s increases, however, the vibrations resemble less and less those of a uniform string, until when $s = \frac{1}{2}(m+1)$ all resemblance disappears, the mode of vibration then being determined entirely by the periodicity of the loading. In other words, as the wave-length of the transverse oscillations is diminished to the point at which it becomes four times the interval between the loads, we are no longer concerned with the behaviour of a uniform string but have to consider, instead, the characteristic vibrations of a periodically loaded string. It may be reasonably inferred from this analogy that in the case of a three-dimensional periodic structure, the ideas based on the physics of continuous media cease to be appropriate in considering vibrations of high frequency in which the atomic architecture of the crystal is specifically involved.

While the specific heat curve can be uniquely derived from the vibration spectrum, a knowledge of the specific heat data is obviously insufficient for a determination of the vibration spectrum. That the Debye formula with an appropriately chosen limiting frequency fits the specific heat data in certain cases is not therefore a proof of the correctness of the basic assumptions of

the theory, and cannot be regarded as an indication that the vibration spectrum in these cases bears any resemblance to that postulated in the theory. It may be recalled that the Debye function is the integrated sum of a continuous sequence of Einstein functions over a range of frequencies with weights proportional to their squares and a sharp cut-off at an upper limit. Experimental data which fit a Debye function should therefore equally be capable of being represented as the sum of a finite number of Einstein functions with appropriate frequencies and weight factors. It is very significant also from our present point of view, that the Debye formula fails to represent correctly the specific heat of several elements crystallising in the cubic system. For, this indicates that the success of the formula in other cases is largely accidental. A feature of the Debye theory which is often emphasised is that the elastic constants calculated from the specific heats come out of the right order of magnitude. As was pointed out in Einstein's earliest papers, however, the existence of approximate relations between the atomic frequencies and the elastic constants is indicated by elementary considerations. No special significance can therefore attach to this feature of the Debye theory.

4 Born's Theory of the Cyclic Lattice

While the Debye theory ignores the discrete structure of the crystal, the crystal dynamics of Max Born and his school formally takes account of it. Born's theory, however, rests on his postulate of the "cyclic lattice", in other words on his assumption that all the atomic displacements are periodic in a volume having the same shape as the elementary cell of the lattice but of very great size in comparison with it. The postulate makes no distinction between the atomic vibrations of high frequency and the elastic vibrations of low frequency, and assumes that all the possible vibrations have wave-lengths which are sub-multiples of the external dimensions of the crystal. It is readily seen that this postulate is unjustifiable. While the external boundary of the solid acts as a reflecting barrier for the elastic waves and thereby determines the frequencies of elastic vibrations, it can have no such influence on the internal vibrations of the crystal lattice. These latter have frequencies which are determined by the crystal structure, and as they do not involve the movement of extended volumes of the material, they cannot either disturb or be disturbed by the conditions at the external boundary of the crystal. Further, the space-patterns of the characteristic vibrations of the lattice are prescribed by the crystal structure, the repetition units being either the same as the lattice spacings or integral multiples thereof. The assumption that the lattice vibrations have wave-lengths which are sub-multiples of an arbitrarily assumed external dimension of the crystal is therefore wholly inappropriate. For these reasons, the Born postulate cannot possibly represent the actual

state of affairs in a crystal. It is evident, in fact, that the Born theory is based on concepts derived from the macroscopic behaviour of elastic solids of the same kind as the theory of Debye which we have already examined and rejected. It follows that the Born crystal dynamics and its consequences must also be considered as unacceptable.

5 *The Spectroscopic Evidence*

It is an essential feature of both the Debye and Born theories that the vibration frequencies of a crystalline solid form a continuous spectrum. This is assumed *ab initio* in the Debye theory, while it follows as a necessary consequence of the postulate of the cyclic lattice on which the Born dynamics is based. The vibration spectrum in the Born theory is divided into the so-called acoustical and optical branches, but it would seem that this distinction does not correspond to any recognisable differences in spectral character. Both the acoustical and optical branches appear as continuous spectra, both have "transverse" and "longitudinal" frequencies, and they also overlap over extensive ranges of frequency. As a typical example illustrating the behaviour of crystals assumed in the Born theory, we may quote the calculations and graphical representations of the vibration spectrum of rock-salt contained in a recent paper by Kellermann (*Phil Trans*, May 1940). It will be seen that the features there shown stand in the sharpest contrast with those indicated by the theoretical considerations put forward in the present paper, namely that the infra-red and elastic vibration-spectra appear in quite different frequency ranges, that the infra-red spectrum consists entirely of discrete or monochromatic frequencies, while the elastic vibrations form a continuous spectrum.

Several experimental methods of studying the frequency spectrum of crystal lattices are available at the present time. A method applicable to all transparent crystals and covering the whole frequency range is the spectroscopic analysis of the scattered radiations emerging from a crystal when it is traversed by a beam of monochromatic light*. A striking and quite general feature emerging from such studies is the *sharpness* of the lines of displaced frequency appearing in the spectra which represent the infra-red vibrations of the solid. These lines are usually quite as sharp as the lines of the incident radiation. This is the case both when the lines represent the extensional or distortional vibrations of the ions or molecules in the crystal lattice, as also when they represent translational or rotational movements. Vibrations of the latter kind which are usually of low frequency are specially

* This field of research is reviewed in an article in the *Journal of the Franklin Institute* for September 1941.

characteristic of the crystalline state. Even in those cases where such lines show an appreciable width at ordinary temperatures, they sharpen to the finest possible lines when the crystal is immersed in liquid air. Such lines fail to appear when the substance is in the amorphous or fluid state, being then replaced by diffuse continua, thus clearly showing that the monochromatism of the vibrations is a consequence of the regular lattice structure of the crystal. As examples proving that the behaviour of actual crystals bears no resemblance to that assumed in the Debye and Born theories, we may mention the cases of the elementary solids, *e.g.*, diamond, sulphur and white phosphorus, as also simple ionic structures, *e.g.*, rock-salt. Every one of these crystals shows well-defined lines in the spectrum of the light scattered by it.

The luminescence of crystals excited by light or by electronic bombardment is another avenue of approach to the study of their lattice spectra. In this case, the transitions between the infra-red energy levels occur in combination with the electronic transitions. The method is therefore applicable for the study of the lattice spectra only when the levels of the electronic transitions are sharply defined. To secure this result, it is usually necessary to cool the crystal to liquid air or even to liquid hydrogen temperature. The subsidiary bands arising from the combinations of the electronic with the infra-red transitions are then found to be quite sharp. Various cases of this kind may be mentioned, *e.g.*, the luminescence of crystals due to atoms of chromium or of the rare earths embedded in their lattices, and the luminescence of the uranyl salts. Recently, it has been found by Nayar working in the laboratory of this Institute that the luminescence of diamond is also resolvable into discrete frequencies at low temperatures, thus enabling its lattice spectrum to be determined. The evidence derived from all such studies points conclusively to the monochromatic nature of the infra-red vibrations characteristic of crystal lattices.

Thirdly, we may mention the avenue of approach to the study of the lattice vibrations provided by the absorption spectra in the visible and ultra-violet. This method is applicable both in the special cases of luminescent crystals and also more generally, *e.g.*, the coloured metallic salts, the salts of the rare earths and organic crystals. Here again, since the infra-red and electronic transitions appear in combination, it is necessary to cool the crystals down to liquid air or even liquid hydrogen temperature before definite information regarding the nature of the lattice spectra can be obtained. The experimental results in such cases as have been fully studied show clearly the monochromatic character of the infra-red vibrations.

Finally, it may be said that the results of infra-red spectroscopy do not contradict the conclusions arrived at by the different methods referred to

above. Much of our knowledge regarding the lattice frequencies of crystals is derived from observations of the reflecting power of crystals for infra-red radiations as a function of wave-length. It is obvious that this method, while yielding useful information, cannot be considered as a method of spectral analysis properly so-called, since the reflecting power does not vanish at frequencies other than those characteristic of the crystal. Absorption methods using very thin plates would evidently be more suitable, but such studies have not been very numerous.

6 Lattice Frequencies and Superlattice Frequencies

The theoretical considerations indicated earlier and the experimental results of spectroscopic research agree in showing that the vibrations of a crystal lattice which appear as monochromatic frequencies in the infra-red spectrum stand in a class apart from the elastic vibrations of macroscopic physics. In considering the relations between crystal properties and crystal structure, we would be justified in ignoring the vibrations of the macroscopic type, since the fraction of the total thermal energy which they carry is negligible. The atomic vibrations appearing in the infra-red spectrum may be classed as lattice vibrations and superlattice vibrations of different orders. The lattice vibrations are those possible when the unit cell of the crystal lattice is the repeating unit in the dynamic space pattern. The term also includes vibrations of the same or nearly the same frequency as the lattice vibrations which arise when superlattices of increasing size are considered as the repeating units. The superlattice frequencies are those which present themselves only when cells of superlattice size are considered. It is evident that they may be roughly pictured as due to the cells of the crystal lattice oscillating against each other in groups. Thus, if a cell of double size and therefore containing 8 lattice cells is the unit of the pattern, the superlattice frequencies of the first order would include 21 out of the 24 degrees of freedom of motion of these 8 cells, while the superlattice frequencies of all the higher orders together would carry only the 3 residual degrees of freedom. The successive orders would thus diminish rapidly in importance. *Pari passu*, their frequencies would diminish owing to the increasing mass of the oscillating units.

As explained above, the superlattice frequencies would be low and would lie in the remote infra-red region of the spectrum. Their contribution to the thermal energy would be small and of importance only at the lowest temperatures. They are, in fact, the nearest analogy in the present theory to the elastic vibrations of macroscopic physics, but differ from them in possessing specifiable frequencies instead of being merely segments in a continuous spectrum. *The existence of monochromatic superlattice frequencies*

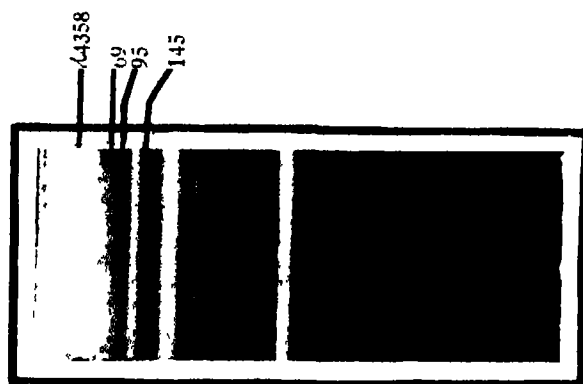


FIG. 1

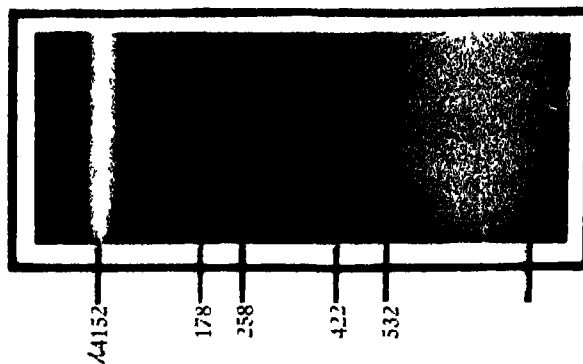


FIG. 2

FIG. 1 Superlattice frequencies in quartz appearing in light scattering

FIG. 2 Superlattice frequencies in diamond appearing in fluorescence

has been established by spectroscopic studies made at this Institute with diamond and quartz These are shown in Figs 1 and 2 in Plate XXXIV. That similar vibrations exist also in other crystals is hardly to be doubted, though lying in the remote infra-red, they would naturally be less easily demonstrable by spectroscopic investigation. In fact, specific heat determinations at the lowest temperatures are probably the easiest way in which their reality can, in general, be proved

7. The Specific Heat Data

The present paper is followed by several others in which the experimental facts concerning the specific heats of various substances of simple composition are examined in detail. These papers speak for themselves. It is sufficient to remark that the results of the examination furnish the clearest experimental proof of the correctness of the new theoretical approach to the problem of the specific heats of solids indicated in the preceding pages

8 Summary

The theory of the specific heats of crystals is considered in this paper from a new standpoint. A crystal being a regular periodic arrangement in space of material particles, the possible vibrations of the atoms in such a structure can be divided into two groups, namely those occurring in a macroscopic scale, and those fundamentally involving the crystal structure. The second group can be further subdivided into lattice vibrations and superlattice vibrations in which the modes of vibration form repeating patterns in space; the unit of this pattern is identical with the lattice cells in one case, and is an integral multiple of its size in the second case. It is shown that the part of the thermal energy associated with the macroscopic or elastic vibrations appearing as a continuous spectrum is entirely negligible. The bulk of the thermal energy is associated with the lattice frequencies properly so called which appear as monochromatic lines in the infra-red spectrum. The residue is associated with the superlattice frequencies of different orders which are also monochromatic. These frequencies appear in the remote infra-red region of the spectrum and their contribution to the specific heat is relatively important only at low temperatures. The spectroscopic evidence regarding crystals is reviewed and shown to be in full accord with these ideas. The specific heat theories of Debye and of Born are critically examined and it is shown that the assumptions on which they are based are theoretically unjustifiable, besides being in contradiction with the experimentally observed behaviour of crystals.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS : WHITE PHOSPHORUS

BY R NORRIS

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

WHITE phosphorus is an elementary solid which crystallises in the cubic system at ordinary temperatures. As its molecular and crystal structure is known, and its spectroscopic behaviour in the Raman effect has been the subject of detailed study, it becomes possible to offer a satisfactory interpretation of its specific heat data.

2 Molecular and Crystal Structure

Dumas (1826) determined the vapour density of phosphorus vapour and found the molecular formula to be P_4 . Beckmann (1890) also found the molecular formula to be P_4 from the boiling point of a solution of phosphorus in CS_2 and this was confirmed by Hertz (1890) from the freezing point of a solution of phosphorus in benzene. Seyler (1884) had earlier arrived at the same conclusion from a consideration of the latent heat of fusion and the specific gravity of the solid and liquid at the melting point. Aston and Ramsay (1894) found that the P_4 formula also agrees with the observed surface tension of the molten liquid, while Smits and Bokhorst (1916) arrived at the same conclusion from the values of the critical constants. Stock and co-workers (1912), by studying the vapour density, found the molecule to continue as P_4 upto 700° , any dissociation that may occur taking place only at still higher temperatures. Bhagavantam (1930) has shown from the Raman effect data that the P_4 molecule must be tetrahedral in form and that the alternative configuration of a square is definitely excluded. The tetrahedral form of the P_4 molecule is confirmed by the study of electron diffraction by phosphorus vapour made by Maxwell, Hendrichs and Mosley (1935). Natta and Passerini (1930), as a result of X-ray investigation of phosphorus at $-35^\circ C$, came to the conclusion that white phosphorus belongs to the cubic system and has 4 P_4 molecules in the unit cell. At still lower temperatures, however, it ceases to be a cubic crystal.

3 Spectroscopic Data

Bhagavantam who was the first to study the Raman effect of white phosphorus reported the presence of only three frequencies at 374, 468 and 607 wave numbers, conforming to a tetrahedral model Venkateswaran (1935) investigated this in greater detail by studying phosphorus in the solid, liquid and vapour states as well as also in solution, and found that a change of state has no marked effect on the Raman lines, except that the frequency at 603 increases by a few wave numbers in going from solid to liquid and from liquid to vapour states He also made (1937) the important observation of the presence of a fairly sharp and intense line displaced by 36 wave numbers from the exciting radiation in the case of solid phosphorus He calculated the frequency of vibration of the phosphorus molecules in the crystal lattice from Lindemann's modified formula to be $\Delta\nu = 27.3 \text{ cm}^{-1}$ Bhagavantam and Venkatarayudu (1938) calculated the modes of vibration of the phosphorus molecule and obtained detailed expressions for the three frequencies by which they identified the 606 frequency to be due to the symmetrical vibration and hence single, 363 to be doubly degenerate and 465 to be triply degenerate, all the three being active in the Raman effect This assignment is in agreement with the observations of Venkateswaran (1937) who had found that in the case of liquid phosphorus, the 606 line is strongly polarised while the other two are depolarised

4 Calculation of the Specific Heat

Considering the 4 P_4 groups in the unit cell of the cubic crystal lattice, we have in all 48 degrees of freedom The P_4 molecule itself has six internal vibrations, of which one is single, one is doubly and the other triply degenerate Of the 48 degrees of freedom, 24 are thus identified with the three discrete Raman frequencies 363, 465 and 606 with their respective degeneracies Amongst the remaining degrees of freedom, 12 must be identified with the three rotational oscillations (triply degenerate) of each of the four P_4 molecules in the unit cell Since the P_4 molecule has tetrahedral symmetry and is located in a cubic cell, it would be optically isotropic and such rotational oscillations would therefore be inactive in the Raman effect Hence, their frequency is not accessible to direct observation Of the remaining 12 degrees of freedom, 3 must be identified with the linear translations of the unit cell as a whole The remaining 9 degrees of freedom may therefore be assigned to the oscillations representing the "hindered translations" of the molecules within the cell The low frequency line at 36 cm^{-1} observed by Venkateswaran in solid phosphorus may reasonably be identified with such translational oscillations of the molecules within the cell This identification appears to be justified by the approximate agreement of this frequency with

that calculated from the Lindemann melting point formula. The alternative interpretation of the 36 cm^{-1} line as due to the rotational oscillation of the molecules is excluded, since such oscillation should be Raman inactive as already explained. Thus we see that of the 48 degrees of freedom of the unit cell, 45 degrees are identified with certain discrete frequencies and hence appear as Einstein terms in the expression for the specific heat of the phosphorus crystal.

The superlattice frequencies must be lower than the observed lowest frequency at 36 cm^{-1} which we have identified as that of translatory oscillation of the molecules. Since the data do not extend to very low temperatures, we shall take the superlattice frequency to be equal to 36 cm^{-1} itself. The frequency of the oscillation corresponding to "hindered rotations" of the P_4 molecules may be expected to be considerably higher. We shall take it as 67 cm^{-1} which is not unreasonably high and gives the best fit with the specific heat data. The gramme-molecular heat of solid phosphorus at temperature T may thus be written as

$$C_v = \left\{ \frac{1}{4} E\left(\frac{\theta_{36}}{T}\right) + \frac{3}{4} E\left(\frac{\theta_{36}}{T}\right) \right\} + \left\{ E\left(\frac{\theta_{67}}{T}\right) \right\} + \\ \left\{ \frac{1}{3} E\left(\frac{\theta_{600}}{T}\right) + \frac{2}{3} E\left(\frac{\theta_{363}}{T}\right) + E\left(\frac{\theta_{465}}{T}\right) \right\}$$

The experimental data concerning specific heat of phosphorus at different temperatures are not available for the several discrete temperatures. However, we have mean specific heats observed between wide temperature intervals between four different temperature regions. These are between (1) 23° to 77° , (2) 82° to 194° , (3) 195° to 271° , and (4) 274° to 290° absolute. The first of these four determinations is due to Dewar (1913), while the other three are due to Ewald (1914). Hence, it will be necessary for comparing the calculated and observed values to calculate the molecular heat in a slightly different manner. Instead of calculating the derivatives of the corresponding energy functions with respect to temperature, we calculate the energy functions themselves. The total thermal energies at two different temperatures T_1 and T_2 being U_1 and U_2 , the mean molecular heat between these two temperatures is

$$C_v = \frac{U_2 - U_1}{T_2 - T_1}.$$

The value of $(C_p - C_v)$ for phosphorus at the room temperature is calculated from the thermodynamic relation to be $= 3.06$, while its values at the other mean temperatures are calculated with the aid of Grüneisen's law as was done by the author (1941) for the case of sulphur. The following table

TABLE
Specific Heat of Phosphorus

T° (Abso- lute)	$\frac{1}{2} U_{E_{s1}}$	$\frac{1}{2} U_{E_{s2}}$	$U_{E_{s7}}$	Uninternal = $\frac{1}{2} U_{E_{s1}} + \frac{1}{2} U_{E_{s2}} + U_{E_{s7}}$	Total U	Mean heat $C_p = \frac{U_2 - U_1}{T_2 - T_1}$	$C_p - C_v$	Total mean heat C_p calcu- lated	Total mean heat C_p ob- served
23	9	27 36	8 9	= 0	45	9 45	0 1	9 55	9 60
77	80	241 5	230 2	(0 02 + 2 526 + 0 685) = 3 231	555				
82	87	262 92	256 6	(0 44 + 3 75 + 1 164) = 4 962	612	14 23	0 775	15 01	15 44
194	251	754 5	894 7	(19 79 + 153 6 + 132) = 305 39	2206				
195	253	760 5	898 56	(20 3 + 156 + 134 4) = 310 7	2223	18 28	2 344	20 62	20 48
271	366	1099 5	1345	(72 9 + 358 + 371) = 801 9	3612	19 63	3 06	22 69	22 0
274	371	1113	1362	(75 6 + 366 6 + 382 3) = 824 5	3670				
290	395	1185	1456	(90 8 + 415 + 442 8) = 948 6	3984				

compares the mean gramme-molecular heat of solid phosphorus thus calculated with the experimentally observed values

It will be seen that the calculated values of the mean molecular heat of phosphorus agree well with the observed values

In conclusion, the author desires to record his grateful thanks to Prof Sir C V Raman, for his kind interest in this work

5 Summary

The specific heat of solid phosphorus is calculated by considering the unit cell of $4 P_4$ molecules. Of its total 48 degrees of freedom, 24 are identified with the internal vibrations of the P_4 molecule identified by their respective Raman frequencies with their appropriate degeneracies, 12 are associated with the inactive frequency of a triply degenerate rotational oscillation of each of the $4 P_4$ molecules, 9 degrees of freedom with the observed low frequency vibration due to the " hindered translations " of the P_4 molecules in the unit cell. All these 45 terms being due to discrete frequencies, their Einstein terms are involved in the calculation of the specific heat. The remaining three degrees of freedom corresponding to the simple translations of the unit cell in the lattice are also assumed to contribute an Einstein term to the specific heat. The values thus calculated are in good agreement with the observed values

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THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: LITHIUM, TUNGSTEN, GOLD, SILICON AND GREY TIN

BY BISHESWAR DAYAL

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

THE success of Debye's formula in representing the variation with temperature of the specific heat of a large number of metals crystallizing in the cubic system has for many years been regarded as conclusive evidence for the correctness of the assumptions on which this theory is based. Gradually, however, various experimental facts have come to light which do not fit into the theory. According to Debye, the specific heat of an elementary solid is expressible as a function involving only one arbitrary constant known as the Debye characteristic temperature for the substance, this constant itself being expressible in terms of the elastic modulus of the solid. Several cases have however come to light in which it is impossible to fit the specific heat data into a formula of this kind. In order to preserve at least the framework of the theory, it has become the fashion to regard the "characteristic temperature" as being itself a function of the temperature and to exhibit its variation graphically. On a close examination of the matter, it is found that there are comparatively few cases in which the "Debye temperature" is even approximately constant over a wide range of temperature. Lead, calcium, molybdenum and vanadium are examples of cases in which a fairly satisfactory fit is obtained. On the other hand, there are equally numerous cases in which the "characteristic temperature" shows quite distinct variations, increasing with the temperature as is the case of gold, diminishing as in tungsten, and in other cases, again, showing more complicated types of variation. In the cases of lithium, grey tin and metallic silicon, the variations are so large that the Debye formula does not even roughly represent the specific heat curve.

An extensive literature has grown up in the attempt to interpret these failures of the Debye theory on the basis of special hypotheses. It is not proposed here to enter into that literature, as we shall consider the whole question from a more general point of view. Debye's identification of the possible atomic movements in a crystal with the elastic vibrations of a continuous solid seems justifiable only when the wave-length of such vibrations is

sufficiently large in comparison with the lattice spacings of the crystal. There appears, however, no reason for assuming that all the possible types of atomic movement can be described in this fashion. Indeed, wherever it has been possible to make a direct experimental study of the question, *e g*, by photographing the Raman spectra, it is found that such an assumption does not correctly represent the facts. The spectroscope, in fact, discloses that the atomic vibrations even in elementary solids, *viz*, diamond, phosphorus and sulphur, exhibit numerous monochromatic frequencies, the position and number of which may be correlated with the crystal structure of the solid. Such methods of optical study are, unfortunately, not open to us in the case of metals. But we have no reason to suppose that a similar situation does not exist in their case as well. It may be recalled that in making the first attempt to develop a quantum theory of specific heats, Einstein (1907), assumed that the vibrations of the atoms in a solid are monochromatic. The difficulty felt by him later (1911) in sustaining this hypothesis, namely that the vibrations of an atom would be highly damped by its reactions with its neighbours, disappears when it is recalled that the characteristic vibrations of the lattice necessarily occur in the same way in all its cells and are therefore undamped. The highly monochromatic character of the frequencies usually exhibited by crystals in the Raman effect is, in fact, a complete vindication of Einstein's original hypothesis.

From the foregoing considerations, it is clear that for the evaluation of the specific heat, we have to find the frequencies of atomic vibration in the crystal and to assign to each such frequency an Einstein function with the appropriate weight factor. The principal Einstein terms relate to the frequencies of vibration in which the lattice cell is the repeating unit of the vibration pattern in space. Further terms would also have to be added to represent the superlattice frequencies for which the vibration pattern in space is a multiple of the size of the lattice cell, as explained more fully in papers by Sir C V Raman and Dr C S Venkateswaran appearing in these *Proceedings*. The elastic vibrations of the solid properly so-called, however, make no sensible contribution to the thermal energy.

2 Relation to Crystal Structure

We may take the basis group in the cases now under consideration to be the unit cube. This contains two atoms in the case of body-centred lattices, four in the case of face-centred ones, and eight in diamond-like structures. The case of the body-centred lattice is the simplest of all. This may be considered as made up of two interpenetrating simple cubic lattices, one of which is formed by the corner atoms and the other by the central atom of the cube. The three translations of the cell as a whole involve three degrees of freedom.

The Einstein frequency would then correspond to the movement of one single cubic lattice against the other and because of the cubic symmetry, this must be triply degenerate. The case of a face-centred lattice is somewhat more complicated. There are four interpenetrating simple cubic lattices to be considered. Here as well, three degrees of freedom relate to the translation of the cell. The remaining nine degrees of freedom are associated with the possible modes of vibration of the four lattices against each other. Since each frequency must be triply degenerate, we are concerned with three Einstein frequencies. In the case of diamond-like lattices, the unit cell of eight atoms is made up of two groups of four each forming a face-centred cubic lattice. Assigning three degrees of freedom to the translations, twenty-one degrees of freedom are left over. There would then be, in general, seven triply degenerate Einstein frequencies.

The evaluation of the Einstein terms in the specific heat thus involves a knowledge of one characteristic frequency for body-centred lattices, three for face-centred ones, and seven for diamond-like structures. Provisionally and for the sake of simplicity, the three frequencies of a face-centred lattice may be replaced by a single representative frequency. In the case of diamond-like structures, the spectroscopic evidence afforded by diamond itself indicates that it is necessary to have at least two representative frequencies, one of these corresponds to an oscillation of the two face-centred cubic lattices against each other; the other frequency may be pictured as an oscillation of the component atoms in each such lattice amongst themselves. Of the total number of degrees of freedom, one half should evidently be assigned to the vibrations of the first type which would naturally have the higher frequency. Three degrees of freedom being assigned to the translations, the remainder are associated with the second and lower frequency.

The three degrees of translatory freedom of the unit cell appear in each case as superlattice frequencies. Taking a superlattice cell whose edge is double that of the unit cell, we assign three degrees of freedom to the translations of the enlarged cell and the remaining 21 degrees of freedom to seven triply degenerate superlattice frequencies. The three reserved degrees can then be passed on to superlattice frequencies of the second order, and so forth. For our present purpose, we may replace the seven superlattice frequencies of a particular order by a single representative frequency and also restrict ourselves to superlattice frequencies of the first two orders. The expressions for the specific heat accordingly reduce to

$$C_v = 3 R \left[\frac{1}{2} E \left(\frac{h\nu_1}{kT} \right) + \frac{7}{16} E \left(\frac{h\nu_2}{kT} \right) + \frac{1}{16} E \left(\frac{h\nu_3}{kT} \right) \right]$$

for body-centred structures

$$C_v = 3 R \left[\frac{3}{4} E \left(\frac{h\nu_1}{kT} \right) + \frac{7}{32} E \left(\frac{h\nu_2}{kT} \right) + \frac{1}{32} E \left(\frac{h\nu_3}{kT} \right) \right]$$

for face-centred structures

$$\text{and } C_v = 3 R \left[\frac{1}{2} E \left(\frac{h\nu_1}{kT} \right) + \frac{3}{8} E \left(\frac{h\nu_2}{kT} \right) + \frac{7}{64} E \left(\frac{h\nu_3}{kT} \right) + \frac{1}{64} E \left(\frac{h\nu_4}{kT} \right) \right]$$

for diamond-like structures,

where E stands for Einstein function. The last two terms in each case refer to the superlattice frequencies of the first and second orders respectively.

Failing spectroscopic data, the frequencies can be evaluated from the specific heat data themselves. The superlattice frequency of the lowest order is obtained from the specific heat data at the lowest temperature where the contribution of other frequencies becomes negligible. Superlattice frequencies of other orders can similarly be found from the specific heat data at intermediate temperatures. The high-temperature specific heats where the contribution of superlattice vibrations is constant give the lattice frequencies. Towards the end of the paper we shall compare the lattice frequencies empirically found with those given by the melting point formula of Lindemann.

In the present paper the author has used the above method for calculating specific heats of several elements crystallizing in the cubic system which do not fit into the Debye theory. In other cases where the Debye theory gives an approximate fit with the experimental values, calculations show that it is always possible to express the specific heats slightly better by the new method. Such calculations have however, not been given here to save space.

3 Specific Heats of Body-Centred Structures

(a) *Lithium*.—Of all the metals having this structure, lithium is the most interesting since no single Debye function will fit the experimental results, the value of θ Debye changing from 328 at low temperatures to 430 at room temperatures. Various hypotheses have been suggested to explain this so-called anomaly, that given by Simon and Swain (1935) being the most discussed. They believe that Li^+ ions are of two different kinds and some heat is taken up in changing one kind into another. The soundness of this assumption has been questioned and their value of θ Debye (510) is not supported by experimental evidence (Pankow, 1936). Fuch (1936) has tried to explain the specific heats on the assumption of anisotropy, but the values of θ Debye calculated by him on that basis show an even larger deviation than is experimentally the case. The values of the specific heat calculated by us (given below), however, are very close to the experimental values at all temperatures. It is noteworthy also that our Einstein frequency comes very close to that given by Lindemann's melting point formula.

The values of C_v have been taken from the paper by Simon and Swain (*loc cit*) Beutler and Levis' (1934) results have not been used because the accuracy claimed by them is not very high, only the first place of decimals being shown

TABLE I
Specific Heats of Li in Cals/deg gm. atom
 $\nu_1 = 8.4 \times 10^{12}$, $\nu_2 = 4.64 \times 10^{12}$, $\nu_3 = 1.84 \times 10^{12}$
Experimental Data of Simon and Swain (1935)

Absolute temperature	Einstein contribution ν_1	Einstein contribution ν_2 and ν_3	Calculated C_v	Observed C_v	Difference observed - calculated	Debye function $\theta = 350$	Difference observed C_v - Debye C_v
15		0364	0364	045	+ 009	037	+ 008
20		095	095	095	+ 000	087	+ 008
25		173	173	169	- 004	169	+ 000
30	001	278	279	273	- 006	289	- 016
35	0046	4112	416	413	- 003	452	- 039
40	0133	567	580	573	- 007	652	- 079
45	0327	7376	770	770	+ 000	884	- 114
50	064	910	974	995	+ 021	1 137	- 142
60	169	1 239	1 41	1 42	+ 01	1 67	- 45
70	324	1 525	1 85	1 87	+ 02	2 197	- 327
80	509	1 757	2 27	2 31	+ 04	2 67	- 36
90	71	1 948	2 66	2 67	+ 01	3 09	- 42
100	906	2 104	3 01	3 02	+ 01	3 46	- 44
110	1 093	2 228	3 32	3 32	+ 000	3 77	- 45
120	1 269	2 330	3 60	3 59	- 01	4 02	- 43
140	1 569	2 479	4 05	4 01	- 04	4 45	- 44
160	1 813	2 586	4 40	4 34	- 06	4 75	- 41
180	2 006	2 656	4 66	4 57	- 09	4 98	- 42
200	2 156	2 724	4 88	4 78	- 10	5 14	- 36
240	2 372	2 793	5 17	5 28	+ 11	5 36	- 08
280	2 518	2 844	5 36	5 31	- 05	5 52	- 21
300	2 575	2 860	5 44	5 39	- 05	5 63	- 24

(b) *Tungsten*—This is the only metal for which the frequency spectrum has been worked out on the Born-Karman model (Fine, 1939) An approximate method which involved a solution of 140 cubic equations and in which the interaction of an atom and its fourteen neighbours only was considered, was used. The values calculated on that basis do not however show any distinct improvement on those calculated by Debye's formula for $\theta = 310$.

The agreement of the calculated values with Lange's data is excellent. The small deviations with respect to Zwicker's data are well within the experimental errors This is shown by the considerable differences between the two series of measurements made by him in the region of temperatures given below.

TABLE II

Specific Heats of W in Cals/deg gm atom

$$\nu_1 = 5.4 \times 10^{12}, \nu_2 = 4.48 \times 10^{12}, \nu_3 = 1.67 \times 10^{12}$$

Experimental Data of Lange (1924) from 26–91° A and Zwicker (1929) from 100–300° A

Absolute temperature	Einstein contribution ν_1	Einstein contribution ν_2 and ν_3	Calculated C_v	Observed C_v	Difference observed – calculated	Debye function $\theta = 310$	Difference observed C_v – Debye C_v
26.01	013	224	237	213	–.024	272	–.059
32.3	0617	387	449	434	–.015	506	–.072
38.8	165	587	752	750	–.002	826	–.076
46.7	355	866	1.22	1.21	–.01	1.28	–.07
54.7	592	1.144	1.74	1.80	+ .06	1.77	+ .03
74.4	1.176	1.701	2.88	2.87	–.01	2.85	–.02
78.3	1.272	1.797	3.07	3.07	± .00	3.03	+ .04
84.2	1.42	1.908	3.33	3.33	± .00	3.29	+ .04
91.1	1.576	2.026	3.60	3.60	± .00	3.55	+ .05
100	1.745	2.156	3.90	3.77	–.13	3.85	+ .08
200	2.592	2.741	5.33	5.30	–.03	5.30	± .00
300	2.796	2.869	5.67	5.87	+ .20	5.65	+ .22

4. Specific Heats of a Face-Centred Structure

Gold—The specific heats of this metal have been measured by Clusius and Harteck (1928) and unlike most other metals of this structure are not expressed by one Debye function. The values of θ Debye vary between 160 and 186

TABLE III

Specific Heats of Gold in Cals/deg gm atom

$$\nu_1 = 3.14 \times 10^{12}, \nu_2 = 1.80 \times 10^{12}, \nu_3 = 1.15 \times 10^{12}$$

$$C_p - C_v = 2.09 \times 10^{-5} C_p T$$

Experimental Data of Clusius and Harteck (1928)

Absolute temperature	Einstein contribution ν_2 and ν_3	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed – calculated	Debye function $\theta = 163$	Difference observed C_v – Debye C_v
14.96	351	.0195	371	357	–.014	354	+ .003
15.73	389	.029	418	431	+ .013	.408	+ .023
20.33	618	.158	776	782	+ .006	.816	–.024
24.9	8057	.3945	1.200	1.252	+ .052	1.32	–.068
32.5	1.0461	.9575	2.004	1.998	–.006	2.184	–.186
44	1.207	1.840	3.047	3.034	–.013	3.27	–.236
63.6	1.3243	2.8642	4.189	4.144	–.045	4.39	–.246
82.5	1.400	3.414	4.814	4.706	–.108	4.938	–.232
105	1.434	3.759	5.193	5.128	–.065	5.158	–.030
147.5	1.460	4.101	5.561	5.578	+ .017	5.604	–.026
176.5	1.468	4.206	5.674	5.706	+ .032	5.71	–.004
212.5	1.476	4.283	5.759	5.762	+ .003	5.782	–.02

The deviations of the calculated values from the observed data are smaller than those of the Debye function and are not, as is the case with the latter in the same direction throughout. They are however larger than those observed with the body-centred structures. This is possibly due to the fact that we have taken a single Einstein frequency as a representative of a group of three, which may be different from one another.

5 Specific Heats of Diamond-like Structures

(a) *Metallic Silicon*—Specific heats of this substance have been measured at six temperatures by Nernst and Schwes (1930) (20–90° K, by Anderson (1930) (61–296° K, and by Magnus (1923) (138–1000° K. The Debye characteristic temperatures necessary to explain these results vary between 440 and 715. Nernst and Schwes' values are considerably (2–30)% lower than those extrapolated by Anderson from his own data. We have used the latter's extrapolated values in Table IV. $C_p - C_v$ has been calculated by the usual formula from the compressibility (325×10^{-12}), linear coefficient of expansion (7.15×10^{-6}) and C_p at 296 (4.652), the former two being taken from the *International Critical Tables*.

With reference to the distinctly noticeable deviation at 296.3°K, it must be pointed out that Anderson does not claim a very high degree of accuracy for his work. The observed values of specific heats deviate considerably from those given by his curve in this region of temperature. Similar deviations take place at very low temperatures. The order of error can be judged from the fact that the specific heat given by him by interpolation at 65.6° K is 920, while his own determination at a slightly lower temperature (65.1) is 974. The small deviations from Magnus' data are not unexpected, since his values differ by about 4% from Anderson's at the temperatures 297 and 296.3° nearly common to both sets of observations.

(b) *Grey Tin*—The calculation of $C_p - C_v$ requires the exact knowledge of the specific heat, compressibility, coefficient of expansion and density at one and the same temperature. For grey tin only the density and the mean coefficient of expansion between –163 and 18° C are known. We have therefore calculated the values of $C_p - C_v$ by an approximate formula of Grüneisen $\frac{C_p}{C_v} = 1 + 2\gamma T$, where γ is the coefficient of expansion, on the supposition that the coefficient of expansion is the same at all temperatures. γ is taken as 1.59×10^{-6} .

The specific heats were expressed by Lange (1924) by two Debye functions $\frac{1}{2}$ Debye 280 + $\frac{1}{2}$ Debye 76. In terms of one Debye function the θ Debye ranges from (140–225° K.

TABLE IV

Specific Heats of Metallic Silicon in Cals/deg gm atom

$$\nu_1 = 14.7 \times 10^{12}, \nu_2 = 6.59 \times 10^{12}, \nu_3 = 3.66 \times 10^{12}, \nu_4 = 1.30 \times 10^{12}$$

$$C_p - C_v = 1.84 \times 10^{-5} C_p^2 T$$

Experimental Data Extrapolated from Anderson (20.1–89.8) Anderson (89.8–296.3), Magnus (350–1000)

Absolute temperature	Einstein contribution ν_2 and ν_4	Einstein contribution $\frac{9}{8} \text{ RE } \left(\frac{315}{T} \right)$	Einstein contribution $\frac{12}{8} \text{ RE } \left(\frac{705}{T} \right)$	Calculated C_v	Observed C_v	Difference observed – calculated	Debye function $\theta=440$	Difference observed – Debye C_v
20 1	0527			0527	042	0107	044	002
28 2	1174	0038		121	123	+ 002	122	+ 001
39 7	2351	0506		286	336	+ 050	336	+ 000
53 1	3650	210	0009	576	-630	+ 054	752	- 122
65 6	4575	4305	0076	896	920	+ 024	1 255	- 335
89 8	5682	8741	073	1 515	1 495	- 02	2 27	- 775
116 7	6327	1 0178	1205	1 731	1 695	- 036	2 61	- 915
145 5	6690	1 2573	2605	2 151	2 152	+ 001	3 207	- 1 055
158 8	6826	1 5506	5845	2 804	2 740	- 064	3 97	- 1 23
165 8	6864	1 6271	7095	3 019	2 993	- 016	4 18	- 1 187
186 9	6976	1 667	7875	3 141	3 156	+ 015	4 29	- 1 134
199 2	7032	1 7696	1 0225	3 490	3 496	+ 006	4 58	- 1 1084
213 6	7085	1 821	1 1485	3 673	3 684	+ 011	4 73	- 1 046
237 5	7150	1 8709	1 289	3 868	3 841	- 027	4 866	- 1 025
253 3	7187	1 9313	1 497	4 143	4 076	- 067	5 05	- 974
283 3	7236	1 9654	1 6225	4 307	4 335	+ 028	5 144	- 809
296 3	7258	2 0209	1 820	4 565	4 566	+ 001	5 30	- 734
350	7308	2 0378	1 896	4 660	4 534	- 126	5 347	- 813
500	7380	2 088	2 1445	4 963	4 972	+ 009	5 525	- 553
700	7408	2 1603	2 295	5 428	5 298	- 130	5 73	- 432
1000	7423	2 071	2 738	5 550	5 558	+ 008	5 835	- 277
		2 214	2 8556	5 808	5 622	+ 186	5 898	- 276

TABLE V
Specific Heats of Grey Tin in Cals/deg gm atom
 $\nu_1 = 5.44 \times 10^{12}$, $\nu_2 = 2.20 \times 10^{12}$, $\nu_3 = \nu_4 = 0.77 \times 10^{12}$
Experimental Data of Lange (1924)

Absolute temperature	Einstein contribution ν_2 and ν_4	Einstein contribution $\frac{9}{8} RE \left(\frac{105}{T} \right)$	Einstein contribution $\frac{12}{8} E \left(\frac{260}{T} \right)$	Calculated C_v	Observed C_v	Difference observed - calculated C_v	Debye function $\theta = 140$	Difference observed C_v - Debye C_v
15.5	471	1168		588	599	+ 011	599	000
18.2	534	2335		768	755	- 013	909	154
22.35	5899	4568	004	1 051	1 056	+ 005	1 45	394
26.8	6357	7088	017	1 363	1 375	+ 009	2 04	665
31.5	6645	9488	053	1 666	1 675	+ 009	2 63	955
37.3	6864	1 1966	136	2 019	2 00	- 019	3 23	- 1 23
44.9	704	1 443	307	2 45	2 36	- 09	3 83	- 1 47
52.3	714	1 612	518	2 84	2 80	- 04	4 27	- 1 37
59.3	721	1 731	.734	3 19	3 14	- 05	4 58	- 1 44
69.5	727	1 850	1 039	3 62	3 67	+ 05	4 91	- 1 24
92.5	735	2 007	1 602	4 34	4 42	+ 08	5 33	- 1 91
102.6	737	2 05	1 799	4 59	4 73	+ 14	5 44	- 1 71
283.6	743	2 208	2 776	5 72	6 08	+ 36	5 88	+ 20

6. Remarks on the Frequencies Assumed

In Table VI the values of the lattice frequencies obtained from the specific heat data are compared with those deduced from the Lindemann melting point formula. The following form given by Grüneisen in his article in the "Handbuch der Physik" has been used

$$\nu = 2.5 \times 10^{12} \sqrt{\frac{T_s}{AV_0^{2/3}}}$$

where T_s = melting point in absolute degrees, A = atomic weight and V_0 = atomic volume.

TABLE VI
Comparison of Frequencies

Substance	ν from Lindemann formula		Einstein ν from specific heat data	
	ν	$\theta = \frac{h\nu}{K}$	ν	$\theta = \frac{h\nu}{K}$
		deg K		deg K
Lithium	8.7×10^{12}	417	8.4×10^{12}	400
Tungsten	5.23×10^{12}	251	5.4×10^{12}	260
Gold	3.34×10^{12}	160	3.14×10^{12}	350
Silicon	8.51×10^{12}	407	6.59×10^{12}	315
Grey tin	1.86×10^{13} *	89*	14.7×10^{12}	705
			2.20×10^{13}	105
			5.44×10^{13}	260

* From data for ordinary tin

For the first three metals the frequencies obtained from Lindemann formula are very near to those used by us. In the latter two cases such agreement is not to be expected because two frequencies are involved. The lower of the two frequencies, however, comes near the Lindemann frequency. It is noteworthy that, as in the case of diamond, one frequency is about double the other.

An independent estimate of the higher frequency of silicon can be made by the use of Nagendra Nath's theory of the vibrations of the diamond lattice (1934). His formula for the higher frequency 1332 cm^{-1} of diamond is

$$\nu = \frac{1}{2\pi c} \sqrt{\left[\frac{8}{3M} \left(K + 8 \frac{K' - K'''}{p^2} \right) \right]}$$

which must also hold good for silicon because of the similarity of structure. K , K' and K''' in the formula stand for the force constants for primary valence, directed valence and intravalence, respectively, while M is the mass of the atom and p the distance between any two connected atoms. The second term in the above formula is unknown for silicon but is comparatively small (about 30% of the first) for the force constants used by Nagendra Nath for carbon. The value of K for silicon has been found to be 1.7×10^8 dynes/cm.

by Still and Yost (1937) from the Raman spectrum of disilane. The corresponding value of K for carbon from a compound of similar structure is 4.64×10^5 dynes/cm. If the latter value is put in the above formula for diamond, the first term by itself (neglecting the other) gives the frequency as 1308 cm^{-1} which is near the observed value. We shall therefore not be far wrong in calculating the frequency for silicon in the same way from the value K and neglecting $\left(\frac{K' - K'''}{p^2}\right)$. The frequency thus obtained is 516 cm^{-1} which is not so different from the 491 cm^{-1} adopted for the specific heat calculations. An alternative method of calculation is to assume that

$$\frac{\nu_{\text{silicon}}}{\nu_{\text{carbon}}} = \sqrt{\frac{M_{\text{carbon}} \times K_{\text{Si}}}{M_{\text{Si}} \times K_{\text{carbon}}}} = \frac{\nu_{\text{Si}}}{1332}$$

which gives us 525 cm^{-1} for ν_{Si} on using the values of K quoted above.

In conclusion the author wishes to thank Professor Sir C. V. Raman, Kt, FRS, NL, for his guidance and encouragement.

7 Summary

It is shown in the paper that the specific heat formula for all metals must necessarily include two types of Einstein terms, one corresponding to the lattice frequencies and the other to the superlattice frequencies. The number of lattice frequencies is shown to be one in the case of body-centred cubic lattices, three in the case of face-centred cubic types and seven in diamond-like structures. In the latter two cases the groups of frequencies have been replaced for simplicity by one and two representative frequencies respectively. The specific heats of the so-called anomalous cases, Li, W, Au, Si and grey tin have been calculated on the above basis and a satisfactory agreement with experimental results has been obtained. In the first two types of structures the monochromatic lattice frequencies obtained are shown to be of the same order as those given by Lindemann's melting point formula.

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THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: DIAMOND

BY V B ANAND, M Sc

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

DIAMOND is the outstanding example of an elementary substance in the solid state which shows an abnormally low specific heat at ordinary temperatures rising to the normal value at very high temperatures. The measurements of specific heat by Weber (1875) made with diamond exhibiting this phenomenon enabled Einstein (1907) to make a test of the quantum theory of specific heats in his first classic paper on the subject. Later determinations by Dewar (1905) and by Nernst (1911) showed that the specific heat of diamond tends to zero at very low temperatures. These measurements furnished material for a test of the formulæ for specific heat proposed by Nernst and Lindemann (1911) and by Debye (1912). It should be noted that these early theories and discussions were based upon postulates regarding the nature of the vibration spectrum of diamond and not upon any independently ascertained facts regarding the latter. Of late years, however, investigations on the Raman effect, on infra-red absorption and especially the recent studies of Nayar (1941) on the absorption of ultra-violet radiations and the luminescence spectrum of diamond have furnished us with a wealth of information regarding the lattice spectrum of this crystal. The information thus derived definitely contradicts the assumption of Debye that the lattice frequencies of diamond form a continuous spectrum of elastic vibrations bounded by an upper limiting frequency. The actual nature of the vibrations should obviously stand in the closest relation to the crystal structure of diamond. Some light has been thrown on the subject by the investigation of Nagendra Nath (1934) and of Venkatarayudu (1938). Accurate data for the specific heat are also forthcoming from the work of Magnus and Hodler (1926) and especially of Pitzer (1938) over a wide range of temperatures. The time is thus ripe for an attempt to consider the thermal energy data for diamond on a new basis, namely the spectroscopic facts on the one hand and the known crystal structure with its possible modes of vibration, on the other.

2. Experimental Data for Specific Heat

Following the early work of Regnault, Wullner and Bettendorf and De La Rive and Marcet indicating that the specific heat of diamond

increases with the rise of temperature, Weber (*loc cit*) studied such variation over a large range of temperature

Magnus and Hodler (1926) determined the specific heat of diamond at high temperatures. More recently Pitzer (1938) has measured the specific heat of diamond over the temperature range 70°K — 300°K . He took twenty grams of diamonds of a grade known as "bortz". Their heat capacity was believed to be the same as that of perfect diamonds within the limits of observational error. Pitzer points out that the data of Nernst below 100°K are not very reliable. According to Pitzer himself, the error in his results may be as large as 5% at the lowest temperatures where the heat capacity of the diamonds was only about one-tenth of the heat capacity of the empty calorimeter, but it rapidly diminishes to about 0.2% at 150°K . At the highest temperatures the errors are somewhat larger on account of the rapid heat exchange by radiation.

Robertson, Fox and Martin (1934) drew attention to the fact that there are apparently two types of diamond which differ in their spectroscopic behaviour, and (1936) determined the specific heats of the two types to see if they were different. They concluded from their researches that the specific heats were the same within the limits of experimental error.

The values given in the *International Critical Tables* (1926 edition) for the atomic heat at low temperatures are indicated therein to be very uncertain, and it is mentioned that for high temperatures the (recent) data of Magnus and Hodler should be referred to. We shall therefore regard as standard Pitzer's values between 70°K and 288°K and Magnus and Hodler's values for the higher temperatures. These values are shown in Table I.

3 Raman Effect and Infra-Red Absorption

Raman Effect Data—Ramaswamy (1930), as also Robertson and Fox (1930), discovered that diamond exhibits in the Raman effect a spectrum line with a frequency shift of 1332 cm^{-1} . This is so intense that it can be photographed even with a tiny diamond with an exposure of an hour or two. Bhagavantam (1930), who investigated the subject with special thoroughness, found in addition to this intense line, others of very low intensity lying on either side of it. Of these again, the most prominent is the one having the smallest frequency shift, namely 1158 cm^{-1} . The other lines having frequency shifts of 1288, 1382, 1431, 1480 and 1585 cm^{-1} are much weaker, and require large clear diamonds and long exposures to enable them to be recorded. Robertson, Fox and Martin (1934) established that the Raman frequency of 1332 cm^{-1} is the same for diamonds of the two types studied by them. Nayar (1941) has studied the temperature variation of the principal Raman

frequency 1332 cm^{-1} At liquid air temperature, the frequency shift is 1333.8 cm^{-1} , at the room temperature 1332.1 cm^{-1} , at 182°C it is 1331.0 cm^{-1} while at 857°C this is 1316.4 cm^{-1}

Infra-red Absorption — The infra-red spectrum of diamond has been studied by Angstrom, Julius, Reinkober (1911) and recently by Robertson, Fox and Martin (1934). From the selection rules due to Placzek for the lattice vibrations in cubic crystals, it follows that vibrations which are active in the Raman effect should be inactive in the infra-red, and *vice versa*. Hence it follows that the Raman frequency 1332 cm^{-1} should not be observable in infra-red absorption. Actually, however, diamonds of type I exhibit a strong absorption in this region, and it is seen from the data reproduced in the paper of Robertson *et al.*, that the curve exhibits a very steep fall or edge coinciding with 1332 cm^{-1} , that is, with the Raman line. It is therefore evident that the observed absorption is due to the same lattice vibration which gives rise to the Raman-active frequency 1332 cm^{-1} which for some reason (not yet fully understood) is also active in infra-red absorption. Diamonds of type II, according to Robertson *et al.*, do not show this strong absorption at 1332 wave-numbers. Reinkober's curve for such a diamond, however, exhibits a series of small undulations which correspond more or less exactly with the Raman frequencies of diamond noticed by Bhagavantam (*loc cit*), including especially the principal frequency at 1332 cm^{-1} . Reinkober also noticed a weak but significant infra-red absorption at 710 cm^{-1} the limit of which is at 760 cm^{-1} . As no corresponding line is observed in light scattering, it is to be presumed that this is a lattice oscillation which is normally inactive both in light scattering and in infra-red absorption.

4 Luminescence and Ultra-Violet Absorption

The fluorescence and ultra-violet absorption spectra of numerous diamonds have been recently investigated by Nayar (1941) both at room and liquid air temperatures with very interesting results. He finds that all diamonds exhibit an electronic band which becomes very sharp at liquid air temperature, then appearing at 4153 Å . This is seen as a dark line in absorption and as a bright line both in fluorescence and phosphorescence. As a result of combination between this electronic vibration and the lattice vibrations in the crystal, new bands arise which appear with increased frequencies in absorption and with diminished frequencies in luminescence. The differences between the electronic frequency and these subsidiary absorption and emission frequencies enable us to evaluate the lattice frequencies of diamond. Of these bands, by far the most intense are two, shifted from the position of the electronic band by 780 cm^{-1} and 1332 cm^{-1} respectively. These are accompanied by fainter companions adjacent to them with smaller

frequency shifts. The other bands of higher frequencies are very weak and diffuse and may be explained as overtones and combinations. As has been pointed out by Nayar, there is a general correspondence between the lattice frequencies deduced from ultra-violet absorption and luminescence data and from the Raman effect results on the one hand and the infra-red absorption on the other. We are thus clearly justified by the spectroscopic data in assuming that the fundamental lattice vibrations in diamond fall into two groups with representative frequencies 1332 cm^{-1} and 780 cm^{-1} respectively.

5 Vibrations of the Diamond Lattice

The diamond lattice, as is well known, consists of two interpenetrating cubic face-centred lattices, in which each of the carbon atoms belonging to one lattice is bound to its four nearest neighbours in the other lattice at the tetrahedral valence angles. We can recognize in this structure cubic cells with edges 3.561 \AA having four atoms within the cell, six at the centres of the faces and eight atoms at the corners. The eight corner atoms are equivalent to one atom, the six face-centre atoms to three, which with the four atoms inside make eight atoms per unit cell. Of these, the four belonging to one lattice lie within the cell and the remaining four are shared with the neighbouring cells.

The possible modes of vibration of the diamond lattice may be looked at from two entirely distinct points of view. The first would be to ignore the crystalline structure, and following Debye to treat diamond as a continuum traversed by longitudinal and transverse waves. This idea of the continuum would be appropriate only so long as the wave-length of the acoustic waves is many times greater than the largest atomic spacings of the crystal. The considerations of Debye, however, cease to represent the position even approximately when the wave-length of the oscillations considered is not greater than four times the atomic spacing. Vibrations of higher frequencies should be pictured in quite a different way.

Considering the 8 atoms in the cubic cell, we can imagine these to oscillate against each other in such manner that their centre of gravity remains at rest, it being further assumed that the corresponding atoms in all the cells oscillate with the same frequency and phase. Nagendra Nath (1934) has discussed and evaluated the frequency of a particularly simple type of vibration, namely that in which the two interpenetrating face-centred cubic lattices forming the diamond structure oscillate with respect to each other as rigid wholes. He has shown that such a vibration can be identified with that giving rise to the Raman line 1332 cm^{-1} . The expression for the frequency of this line obtained by him may be put in the form

$$\nu = \frac{1}{2\pi} \sqrt{\frac{8}{3M} (K + 8K_a)}, \quad (1)$$

where M is the mass of the carbon atom and K , K_a are force constants denoting primary valence (four nearest atoms) and directed valence respectively. If we give reasonable values to K and K_a , the frequency turns out to be of the same order as the observed Raman frequency of 1332 wave-numbers Venkatrayudu (1938) has shown on the group theory that such an oscillation of the interpenetrating lattices should be active in the Raman effect

Regarding the two interpenetrating face-centred cubic lattices as single units oscillating against each other, it would follow that such oscillation being triply degenerate would represent three out of the six degrees of freedom of such a system. We may therefore assign half the total number of degrees of freedom in the crystal to the group of frequencies of which 1332 cm^{-1} is regarded as representative. The degrees of freedom associated with each unit cell being twenty-four, twelve are thus attached to the 1332 cm^{-1} group of frequencies. The three degrees of freedom of translation of the unit cell would be associated with the superlattice frequencies. Nine degrees of freedom would thus be left over for the group of vibrations of which 780 cm^{-1} is representative. It is worthy of remark that this division of 24 degrees of freedom into 12, 9 and 3 runs parallel to the division of the 8 atoms of the cell into 4, 3 and 1 respectively within the cell, at the face-centres and at the corners. The vibrations of frequency 780 cm^{-1} are no doubt to be described as oscillations of the atoms in each face-centred lattice amongst themselves

6 Superlattice Frequencies

It now remains to associate the superlattice frequencies with the three translations of the unit cell in the crystal. The fluorescence and absorption spectra studied by Nayar exhibit other features besides the intense bands having their heads at 1332 and 780 wave-numbers which we have taken to be representative of the lattice frequencies. Most noticeable amongst these other features is a fairly bright band sharply limited at 532 wave-numbers, and followed by a succession of fainter bands. We shall take the frequency of 532 wave-numbers as representative of the superlattice frequencies of the first order. Nayar's plates also show two feeble bands of approximately equal intensity displaced by 178 and 258 wave-numbers respectively from the electronic band. We shall take the mean of the two, namely 218 as representing the superlattice frequencies of the second order. Of the 24 degrees of freedom of translation of the 8 cells included in the superlattice, 21 are associated with the first order and 3 with the second order. The atomic heat C_v of diamond is accordingly expressed by the formula

$$C_v = \frac{3R}{8} \left[4E\left(\frac{h\nu_1}{kT}\right) + 3E\left(\frac{h\nu_2}{kT}\right) + \frac{7}{8}E\left(\frac{h\nu_3}{kT}\right) + \frac{1}{8}E\left(\frac{h\nu_4}{kT}\right) \right] \quad (2)$$

where $\nu_1, \nu_2, \nu_3, \nu_4$ are respectively 1332, 780, 532 and 218 in spectroscopic units. Here, E denotes the Einstein function, R is the gas constant, h and k are Planck's constant and Boltzmann's constant respectively. The values calculated from relation (2) have been given in Table I.

To compare the calculated values of C_v with the accepted experimental values of C_p , we have to subtract from the observed values the difference ($C_p - C_v$). In the case of Pitzer's data this amounts to 0.001 cal / °C in the last four observations, the difference being even less at lower temperatures. This correction has been made in the values given in the table. Magnus and Hodler have corrected their own data and the values of C_p as given by them, have been reproduced in the table.

TABLE I
Comparison of the Calculated and the Experimental Values

Temp °K	C_v CALCULATED		C_v Observed	Temp °K	C_v CALCULATED		C_v Observed
	Debye's Formula $\nu_m = 1332 \text{ cm}^{-1}$	Spectro- scopic data			Debye's Formula $\nu_m = 1332 \text{ cm}^{-1}$	Spectro- scopic data	
70.16	023	022	022	276.6	1.179	1.247	1.256
75.37	029	029	030	288.0	1.289	1.355	1.354
81.59	036	036	036				
88.65	047	046	045	273	1.143	1.215	1.252
96.68	061	059	059	300	1.405	1.469	1.520
105.1	078	082	079	350	1.898	1.931	1.985
113.0	096	097	099	400	2.362	2.366	2.411
125.3	131	137	138	450	2.786	2.766	2.798
134.3	162	170	174	500	3.164	3.122	3.149
144.1	200	216	218	550	3.489	3.438	3.465
153.7	241	265	267	600	3.768	3.708	3.749
162.8	286	321	318	650	4.013	3.947	3.999
173.3	343	382	386	700	4.223	4.154	4.222
182.0	395	442	444	750	4.405	4.334	4.414
191.4	455	513	518	800	4.554	4.490	4.580
200.9	520	586	595	850	4.694	4.627	4.717
211.8	602	672	685	900	4.811	4.746	4.833
231.1	760	834	858	950	4.910	4.849	4.923
241.1	845	925	918	1,000	5.002	4.946	4.992
252.4	947	1.026	1.032	1,050	5.076	5.030	5.034
264.3	1.057	1.129	1.136	1,100	5.148	5.099	5.060

On comparing the values calculated from Debye's formula ($\nu_m = 1332 \text{ cm}^{-1}$) with those obtained from the spectroscopic data, we notice that till about 100° K. the two results agree closely. Above 100° K. and up to about 400° K. the values given by Debye's formula progressively fall off, the difference between the two calculated values ranging up to as much as 13%.

From 400°K to 1100°K the values according to Debye are consistently higher than those calculated from the spectroscopic data. The difference, however, never exceeds 2%.

When we compare the calculated values with the observed ones, we find excellent agreement between the spectroscopic values and the experimental data throughout the temperature range covered by Pitzer and indeed precisely in the region where the values given by the Debye formula show the largest deviations from the observed ones. This situation is exhibited graphically in Fig 1, the crosses indicating the observed values, while the full line and the

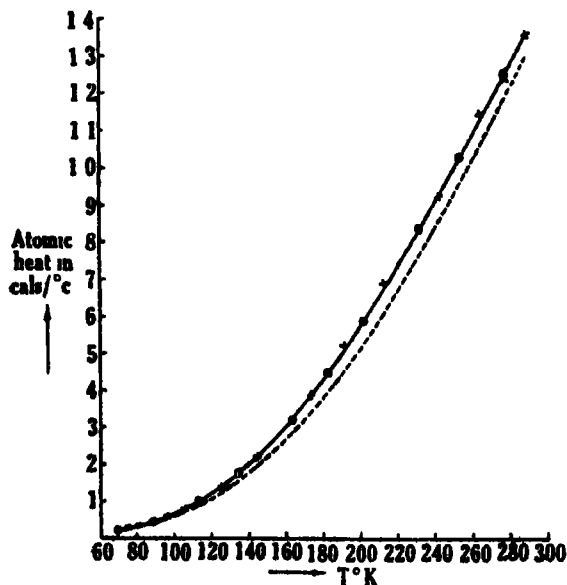


FIG 1

dotted line represent the values calculated from the spectroscopic frequencies and Debye's formula respectively.

The agreement between the spectroscopically calculated atomic heat and the data of Magnus and Hodler is quite good except in the lowest part of the temperature range covered by the work of these authors where the latter are a few per cent higher. It may be remarked, however, that the values of Magnus and Hodler run a little higher than those of Pitzer in this range. It seems possible therefore that Magnus and Hodler's data are systematically a little too high. In any case, little importance can be attached to the small deviations (not larger than about 2%) between the experimental data and the spectroscopically calculated values that appear in the range between 400°K . and 1000°K .; for, on the one hand, Magnus and Hodler have assumed that

the factor A in the semi-empirical formula,

$$C_p - C_v = A C_p^2 T,$$

is constant over the whole range covered by them, and on the other hand, we have not taken into account the lowering of the spectroscopic frequencies with the rise of temperature

In conclusion, the author wishes to record his deep sense of gratitude to Professor Sir C V Raman for his helpful interest and suggestions throughout the preparation of this paper

Summary

It is known that the atomic heat data of diamond are not satisfactorily represented over the entire range (covered by the data) by a single Debye term assuming some one value of the limiting frequency of the elastic spectrum. In the present paper it is shown that the formula fails because Debye's hypothesis does not correctly represent the vibration spectrum of this crystal. The lattice spectrum of diamond is in fact shown by the Raman effect studies of Bhagavantam and the luminescence and ultra-violet absorption spectra studied by Nayar to consist of monochromatic frequencies down to much below the limiting frequency of Debye. The atomic heat data obtained by Pitzer agree perfectly with a formula containing Einstein terms corresponding to the spectroscopically observed frequencies of the lattice, namely 1332 cm^{-1} and 780 cm^{-1} and superlattice frequencies of 532 cm^{-1} and 218 cm^{-1} , their relative weights being 4, 3, $7/8$ and $1/8$ respectively as indicated by dynamical considerations

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THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: MAGNESIUM, ZINC AND CADMIUM

BY BISHESHAR DAYAL

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

IN the form originally given, Debye's theory disregarded the crystalline nature of substances altogether. Its complete failure to account for the specific heats of metals crystallising in the hexagonal system was later ascribed to the anisotropy of single crystals of these substances which would, in general, give a different wave velocity and hence a different limiting frequency for each direction. On a close examination, however, it is found that the specific heat curves of such solids cannot always be represented in such a manner. If we replace the sum of a number of Debye functions by only one such function, but with a variable parameter, the latter would lie closer to the one appearing in the Debye function with lowest parameter at low temperatures, and increase as we go higher up. This is shown in the graph (Fig 1) which represents the sum of two Debye functions ($\theta = 400$ and $\theta = 200$) with only one parameter. The θ Debye curves of zinc and cadmium do show such a behaviour through a large range of temperature in which it increases with temperature. In magnesium, however, the case is just the reverse. It is well known that the Einstein function increases more rapidly as the temperature is raised than the Debye function. The above behaviour of magnesium, therefore, definitely points to the presence of a low-frequency monochromatic oscillation which will increase the specific heat at higher temperatures to a larger extent than would be done by one single Debye function [Cf. Fig 1 where θ_D curve represents the sum of an Einstein function ($\theta = 200$), and a Debye function ($\theta = 250$)]

In an earlier paper of this series the author has shown that the specific heat formula for all metals in the cubic system must necessarily include one or more Einstein functions corresponding to the symmetry of their crystal structure. In the present paper this work is extended to three metals crystallising in the hexagonal system.

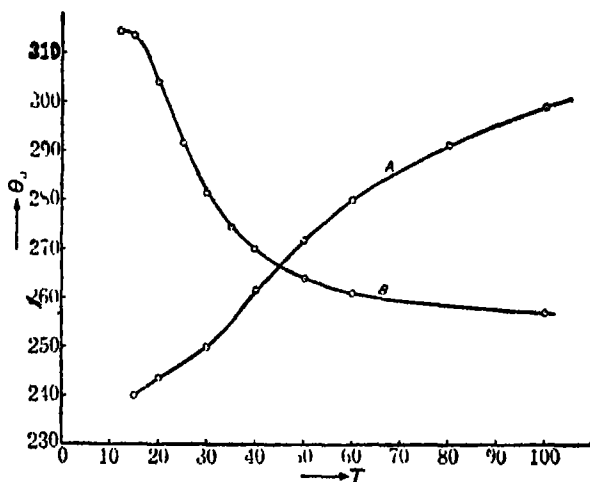


FIG 1

Curve A- θ_D to represent $\frac{3}{2}R \left[D \left(\frac{400}{T} \right) + D \left(\frac{200}{T} \right) \right]$

Curve B- θ_D to represent $\frac{3}{2}R \left[D \left(\frac{250}{T} \right) + E \left(\frac{200}{T} \right) \right]$

2 Relation to Crystal Structure

All the three metals now under consideration have a hexagonal structure in which there are two atoms per unit cell. The positions of the atoms when referred to hexagonal axes are 0, 0, 0 and $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$. There are six degrees of freedom for the basis group, three of which represent the translations of the whole cell in different directions. The remaining three naturally go over to the lattice frequencies, which may be pictured as arising from the mutual oscillations of the two atoms. In the single crystals of these metals, most of the properties such as thermal expansion and elastic constants are strongly anisotropic, the values along the hexagonal axis being completely different from those in directions parallel to the basal plane. In the basal plane itself, no particular axis is favoured. In such a case we are obviously not justified in taking one representative Einstein frequency for all the three degrees of freedom. We have therefore taken two Einstein frequencies, the lower of which corresponding to movements parallel to the hexagonal axis is assigned one degree of freedom, while the higher one is assigned two degrees of freedom. As already explained in the previous paper on metals crystallising in the cubic system, we have also to include the contributions due to a series of superlattice frequencies. For simplicity we will ignore the splitting of these frequencies due to anisotropy. The formula for specific heat then becomes, only four orders of superlattice frequencies being taken,

$$C_p = 3R \left[\frac{1}{3} \left(\frac{h\nu_1}{kT} \right) + \frac{1}{6} \left(\frac{h\nu_2}{kT} \right) + \frac{7}{16} E \left(\frac{h\nu_3}{kT} \right) + \frac{7}{16 \cdot 8} E \left(\frac{h\nu_4}{kT} \right) + \frac{7}{16 \cdot 8 \cdot 8} E \left(\frac{h\nu_5}{kT} \right) + \frac{1}{16 \cdot 8 \cdot 8} E \left(\frac{h\nu_6}{kT} \right) \right]$$

The total contribution of superlattice frequencies is given in the second column of the following tables

3 Evaluation of Specific Heats

(a) Magnesium —

$$\nu_1 = 6.49 \times 10^{12}, \quad \nu_2 = 3.55 \times 10^{12}, \quad \nu_3 = 4.92 \times 10^{12}, \\ \nu_4 = 2.32 \times 10^{12}, \quad \nu_5 = \nu_6 = 1.05 \times 10^{12}$$

(b) Zinc —

$$\nu_1 = 5.23 \times 10^{12}, \quad \nu_2 = 1.92 \times 10^{12}, \quad \nu_3 = 3.35 \times 10^{12}, \\ \nu_4 = 1.47 \times 10^{12}, \quad \nu_5 = 0.88 \times 10^{12}, \quad \nu_6 = 0.36 \times 10^{12}.$$

(c) Cadmium —

Since the values of C_v are not given in the paper of Lange and Simon from which the experimental data are taken, they were calculated by the usual formula

$$C_p - C_v = A C_p^2 T, \text{ where } A = \frac{9 \alpha^2 V}{J k C_p^2}$$

(α = coefficient of linear expansion, V = atomic volume, J = mechanical equivalent of heat, k = compressibility) The constants used were (all to 0°C)

$$k = 2.27 \times 10^{-12}$$

$$C_p = 5.32$$

$$\alpha = 38 \times 10^{-6}$$

$$V = 13.0$$

A was found to be 4.7×10^{-5}

$$\nu_1 = 3.55 \times 10^{12}, \quad \nu_2 = 1.17 \times 10^{12}, \quad \nu_3 = 2.34 \times 10^{12},$$

$$\nu_4 = \nu_5 = \nu_6 = 0.84 \times 10^{12}$$

4. Remarks on the Frequencies Assumed

Table IV compares the lattice frequencies with those obtained from the Lindemann melting point formula. In the case of magnesium, the frequency obtained from the Lindemann melting point formula is practically the same as has been used for specific heat evaluations, but in the other two cases it is nearly equal to the average of the two frequencies. This is presumably connected with the difference in their structure. Magnesium is a close-packed structure representing the way in which a number of spheres could be most densely packed together. The packing in zinc and cadmium on the other hand is rather loose, the axial ratio c/a being much larger than is the case with magnesium. This difference is also reflected

TABLE I Magnesium
Experimental Data of Clusius and Vaughen (1930)

Absolute temperature	Einstein contribution ν_0, ν_1	Einstein contribution ν_1	Einstein contribution ν_1	Calculated C_p	Observed C_p	Difference observed - calculated	Debye function $\theta = 365^\circ$	Difference observed C_p - Debye C_p
11 31	0129			0129	013	+	0135	0005
11 41	0135			0135	013	-	014	001
14 14	0258	0009		027	026	-	027	001
16 94	0436	0044		048	049	+	047	002
19 50	0659	0124		078	075	-	071	004
21 7	0857	024		110	112	+	098	014
27 1	163	074	0029	240	246	+	190	056
30 2	220	114	0073	341	353	+	261	092
34 2	3111	1727	0189	503	533	+	375	358
45 2	6363	3425	0981	1 664	1 720	+	803	419
55 1	9616	4753	2273	2 163	2 206	+	1 292	428
63 7	1 2306	5657	3663	3 269	3 223	-	1 732	474
86 7	1 790	7275	751	3 514	3 515	+	2 818	405
93 2	1 909	7585	846	3 716	3 682	-	3 072	443
99 2	2 004	782	9296	3 942	3 836	-	3 288	394
106 7	2 1108	8073	1 0243	4 164	4 147	-	3 54	296
115 4	2 210	8315	1 1222	4 362	4 363	-	3 79	357
124 2	2 3017	851	1 2087	4 578	4 564	+	4 01	353
136 2	2 396	8719	1 3098	4 712	4 742	-	4 27	294
145 4	2 4486	8855	1 3783	4 938	4 960	+	4 44	302
163 4	2 5475	9083	1 482	5 031	5 071	+	4 71	25
272 6	2 5900	915	1 526	5 127	5 100	+	4 821	25
182	2 6342	9236	1 5687	5 192	5 118	-	4 927	173
191 2	2 6600	9293	1 6023	5 350	5 291	-	5 001	117
217 2	2 7280	9437	1 6787	5 404	5 339	-	5 196	095
228 4	2 7500	9483	1 7053			-	5 26	079

TABLE II: Zinc

Experimental Data of Keesom and Ende (3.2 to 20° K and Clusius and Harteck (21.9 to 201.9° K

Absolute temperature	Einstein contribution $\nu_0, \nu_1, \nu_2, \nu_3$	Einstein contribution ν_2	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed - Calculated	Debye function $\theta = 205$	Difference observed C_v - Debye C_v
3.2	00082	..	.	00082	00093	+ 00011	00177	- 00084
3.6	00118			00118	00122	+ 00004	00253	- 0013
4	00168			00168	00155	- 00013	00347	- 0019
6	00527			00527	00476	- 00051	01170	- 0069
8	0140	0013		0153	0152	- 0001	0278	- 0126
10	0302	00849		0387	0387	± 0000	0542	- 0155
12	0536	0273		0809	0792	- 0017	0933	- 014
16	120	1051		225	219	- 006	221	- 002
18	165	1584	0004	324	327	+ 003	311	+ 016
20	2176	2153	-0012	434	489	+ 055	424	+ 065
21.9	2768	2705	0028	550	537	- 014	543	- 006
26.5	4536	3961	0141	864	899	+ 035	895	+ 004
34.3	8165	5633	114	1494	1514	+ 02	159	+ 085
43.9	1264	696	219	2179	2252	+ 073	2444	- 192
54.2	1650	7845	4282	2868	290	- 032	3198	- 346
71.8	20952	8679	7883	3751	3723	- 028	411	- 387
85.5	2317	903	102	4240	4174	- 066	454	- 366
104.1	2505	931	1255	4691	4611	- 08	4947	- 336
140.9	2707	958	1535	5200	5196	- 004	5368	- 172
154.8	2753	9642	16023	5320	5299	- 021	5466	- 167
178.2	2804	9703	16903	5465	5410	- 055	5558	- 148
201.9	2843	975	1744	5562	5517	- 045	5664	- 147

Since there is no constant θ Debye below 12° K, its value in the column 8 has been taken from the value given by Clusius and Harteck for the T° region (12-20° K). The order of error at low temperatures can be judged from the fact that at 20.09° Clusius and Harteck's value is -421, about 16% less than that given above from Keesom and Ende.

TABLE III *Cadmium*
Experimental Data of Lange and Simon

Absolute temperature	Einstein contribution ϵ_2, ϵ_4	Einstein contribution ϵ_2	Einstein contribution ϵ_1	Calculated C_v	Observed C_v	Difference observed -- calculated	Debye function $\theta = 119$	Difference observed C_v -- Debye C_v
10	117	116	029	233	215	018	216	+ 001
20	575	536	222	1 14	1 12	- 02	1 61	- 49
30	1 248	748	527	2 22	2 25	+ 03	3 03	- 78
40	1 751	845	819	3 12	3 18	+ 06	3 97	- 79
50	2 096	896	1 057	3 81	3 86	+ 05	4 56	- 70
60	3 322	924	1 240	4 30	4 32	+ 02	4 94	- 62
70	2 476	941	1 378	4 66	4 63	- 03	5 18	- 55
80	2 583	953	1 477	4 91	4 84	- 07	5 35	- 51
90	2 647	962	1 567	5 09	5 06	- 03	5 47	- 41
100	2 719	967	1 631	5 25	5 19	- 06	5 56	- 37
110	2 763	971	1 788	5 37	5 28	- 09	5 61	- 33
150	2 856	982	1 869	5 63	5 50	- 13	5 77	- 27
200	2 909	986		5 76	5 60	- 16	5 85	- 25

TABLE IV
Comparison of Frequencies

Substance:	Frequency from Lindemann		Frequency used	
	$\nu \times 10^{12}$	$\theta = \frac{h\nu}{k}$ deg K	$\nu \times 10^{12}$	$\theta = \frac{h\nu}{k}$ deg K
Magnesium	6 31	302	6 49 3 55	310 170
Zinc ..	3 87	185	5 23 1 92	250 92
Cadmium	2 43	116	3 55 1 17	170 56

in the fact that whereas the lower frequency of magnesium is a little more than half of the higher, in the other two cases the ratio of the higher to the lower frequency is 3 : 1 nearly

In conclusion the author wishes to express his grateful thanks to Professor Sir C V Raman, Kt, FRS, NL, for the interest he has taken in the work

5 Summary

The specific heat curves of the metals having hexagonal structure cannot always be expressed in terms of a Debye function even when the anisotropy of the crystals is taken into account. It has been shown that monochromatic Einstein frequencies must be present in order to explain the peculiar shapes of these curves. At least two such frequencies must be present, the smaller of which corresponds to movements of the atoms parallel to the hexagonal axis, the higher to those in the basal plane. The specific heats of such metals can, therefore, be calculated by taking two lattice frequencies, the lower of which is given one and the higher two degrees of freedom. Einstein terms corresponding to superlattice frequencies of rapidly diminishing weight have also to be included. Such calculations have been made for magnesium, zinc and cadmium and are found to show an excellent agreement with experimental results.

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THE THERMAL ENERGY OF CRYSTALLINE SOLIDS : QUARTZ

BY R NORRIS

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

SAXENA (1940) carried out a detailed analysis of the Raman and infra-red spectra of quartz and identified the twenty-four fundamental frequencies of the quartz lattice, assuming that the three silicon and six oxygen atoms forming the basis group vibrate in identically the same way in all the lattice cells of the crystal. Each of the fundamental frequencies of the lattice represents an Einstein function in the expression for the specific heat of the crystal which can therefore be evaluated by summing up the functions. That Saxena's identification of the fundamental frequencies is correct is indicated by the satisfactory agreement of the specific heats thus calculated by him with those experimentally determined over a wide range of temperatures. It is to be remarked that the three degrees of freedom (out of the total of twenty-seven) remaining unrepresented by Einstein terms appear in Saxena's expression for the specific heat as a Debye term. A characteristic Debye temperature of 204° T corresponding to a limiting frequency of 142 cm^{-1} was chosen by him as giving the best fit with the experimental data, without considering the question whether this assumption could be reconciled with the known elastic constants of quartz.

In view of the rather arbitrary choice of the Debye limiting frequency made by Saxena, the specific heat data of quartz are further examined in the present paper. The situation is best exhibited by deducting from the observed specific heats the sum-total of the contributions of the 24 Einstein terms and comparing the differences thus obtained with the Debye function assumed. The tabulations necessary for this purpose are made in Table I. Here the specific heats in calories per gram molecular weight (180.9 gm for 3 SiO_2) are shown, the data from 25° T to 36° T being taken from the early work of Nernst, the values from $53^{\circ}\cdot 4\text{ T}$ to 296° T from the recent work of Anderson (1936), and the values at still higher temperatures from the observations of Moser (1936). The last column of Table I thus shows the residual specific heat due to the three unassigned degrees of freedom. It will

TABLE I

1	2	3	4	5	6
Absolute temperature T°	Total specific heat C_p observed	$C_p - C_v$	Total specific heat C_v observed	Internal vibrations contribution $C_{v_i} - \sum_1^{24} RE \left(\frac{h\nu_i}{kT} \right)$	$C_{v_o} - C_{v_i}$
25 8	1 25		1 25	0 17	1 08
28 75	1 56		1 56	0 28	1 28
31 2	1 58		1 58	0 40	1 18
36 1	2 38		2 38	0 69	1 69
53 4	4 65		4 65	2 05	2 60
60 3	5 56		5 56	2 71	2 85
80 0	8 58		8 58	4 63	3 95
98 9	11 04		11 04	6 70	4 34
122 1	14 29		14 29	9 33	4 96
156 2	18 69		18 69	13 12	5 57
184 8	21 99		21 99	16 09	5 90
216 1	25 07		25 07	19 08	5 99
252 1	28 49	0 15	28 34	22 20	6 14
272 0	30 54	0 20	30 34	23 76	6 58
296 1	31 74	0 25	31 49	25 56	5 93
316 5	33 84	0 27	33 57	26 97	6 60
381 1	37 24	0 40	36 84	30 85	5 99
428 8	39 66	0 50	39 16	33 18	5 98
475 8	41 88	0 63	41 25	35 04	6 21
565 3	45 54	1 00	44 54	37 86	6 68
670 0	48 56	1 74	46 82	40 26	6 56
777 3	52 71	4 03	48 68	41 84	6 84
808 6	54 95	5 88	49 07	42 21	6 86

be noticed that this reaches the limiting value of 5.96 at about $200^{\circ} T$, remains approximately constant upto about $428^{\circ} T$ and then definitely rises beyond the limit at higher temperatures. The last column of Table I is carried over to the second column of Table II for comparison with the theoretical values obtained in different ways. In column three are shown the values calculated from the Debye function assumed by Saxena. It will be seen that over the range from $31^{\circ} T$. to $122^{\circ} T$. these are definitely in excess of the observed values by ten to twenty-five per cent. In the hope of finding an explanation for this discrepancy, the present author has evaluated the Debye limiting frequency from the known elastic data for quartz in different directions. The characteristic temperature calculated in this way comes out to be $271^{\circ} T$. corresponding to a limiting frequency of 189 cm^{-1} . The values of the corresponding Debye function are tabulated in column four of Table II. It will be seen that the situation is now reversed, the calculated values being considerably smaller than the experimental values. The differences become larger as we approach the lower end of the temperature range covered by Anderson's experimental data, while the calculated values are altogether too small in

TABLE II

1	2	3	4	5
Absolute temperature $T, ^\circ$	Observed $C_v - C_{v_j}$	3 RD $\left(\frac{204}{T}\right)$	3 RD $\left(\frac{271}{T}\right)$	RE $\left(\frac{h\nu_1}{kT}\right)$ + 2 RE $\left(\frac{h\nu_2}{kT}\right)^*$
25 8	1 08	0 85	0 39	0 74
28 75	1 28	1 10	0 53	0 95
31 2	1 18	1 32	0 66	1 14
36 1	1 69	1 78	0 96	1 52
53 4	2 60	3 16	2 14	2 78
60 3	2 85	3 57	2 57	3 19
80 0	3 95	4 40	3 57	4 07
98 9	4 34	4 87	4 20	4 61
122 1	4 96	5 20	4 72	5 02
156 2	5 57	5 48	5 14	5 36
184 8	5 90	5 61	5 36	5 52
216 1	5 99	5 70	5 52	5 63
252 1	6 14	5 77	5 62	5 71
272 0	6 58	5 79	5 68	5 76
296 1	5 93	5 81	5 71	5 78
316 5	6 60	5 83	5 74	5 80
381 1	5 99	5 87	5 81	5 85
428 8	5 98	5 89	5 84	5 86
475 8	6 21	5 90	5 86	5 87
565 3	6 68	5 92	5 88	5 90
670 0	6 56	5 93	5 91	5 90
777 3	6 84	5 93	5 92	5 91
808 6	6 86	5 93	5 92	5 92

* ν_1 is a superlattice frequency 69 cm^{-1} and ν_2 is another superlattice frequency 145 cm^{-1} (in spectroscopic units)

the range covered by the data of Nernst. It is thus evident that the Debye function calculated from the elastic constants altogether fails to represent the specific heat at low temperatures

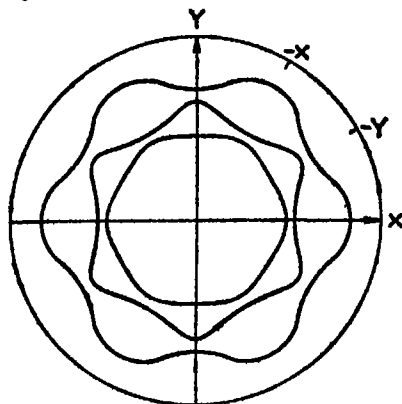


FIG 1
Schaefer-Bergmann pattern for quartz

2 Calculation of the Debye Limiting Frequency

The total number of vibrations whose frequencies lie between ν and $\nu + d\nu$ in an anisotropic solid of volume V is according to Born

$$dz = V F \nu^3 d\nu,$$

where $F = \int \left(\frac{1}{C_1^2} + \frac{1}{C_2^2} + \frac{1}{C_3^2} \right) d\Omega$, the integral being taken over the complete solid angle of 4π . Here C_1 , C_2 and C_3 are the three elastic wave velocities associated with the particular direction, as given by the three real roots of the secular equation of the third degree due to Christoffel. The Debye limiting frequency is thus given by $\nu_m = \sqrt[3]{\frac{9N}{VF}}$. Thus, if the integrand appearing in the expression for F is averaged over the whole solid angle of 4π and if this average is $\frac{1}{C_m^2}$, then the limiting frequency can be written as

$$\nu_m = \sqrt[3]{\frac{9NC_m^3}{4\pi V}}$$

The value of $\frac{1}{C_m^2}$ can be found making use of the diffraction patterns given by a quartz crystal vibrating at ultrasonic frequencies. These patterns have been obtained by Schæfer and Bergmann (1935) in the form of three curves whose radii vectores are proportional to the reciprocal of the velocities of the elastic waves along the respective directions. The scale of the curves can be evaluated with the aid of the known velocities along particular directions, such as the X, Y and Z axes. This can be done by solving the Christoffel equation and using the known values of the six elastic moduli of quartz. The latter have been determined by Voigt by numerous experiments to be $C_{11} = 854.6$, $C_{33} = 1056.2$, $C_{44} = 571.2$, $C_{12} = 72.5$, $C_{13} = 143.5$, $C_{14} = 168.2$, expressed in 10^9 dynes per sq cm. It may be remarked here that Bechmann (1934) has also found the velocities of the elastic waves in quartz along certain directions, by measuring the characteristic frequencies of piezoelectrically excited plates of the crystal.

Figs 1 to 5 represent the Schæfer-Bergmann patterns given by quartz for five different orientations of the crystal. These figures have been drawn making use of the drawings and photographs reproduced in their paper for three cases out of the five. Various alterations have however had to be made in the diagrams given by Schæfer and Bergmann which did not correctly represent the situation as found from the Christoffel equation and Voigt's elastic constants. Fig 1 represents the pattern for a plate cut normal to the triad axis, while Figs 2, 3, 4 and 5 refer to a plate parallel to the triad axis, but inclined to the XZ planes at angles of 0° , 10° , 20° and 30° respectively.

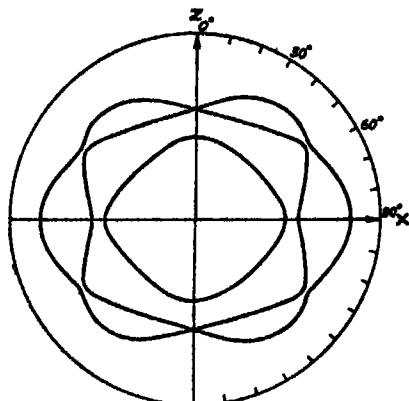


FIG. 2

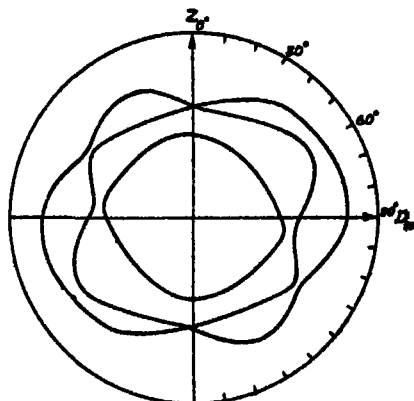


FIG. 3

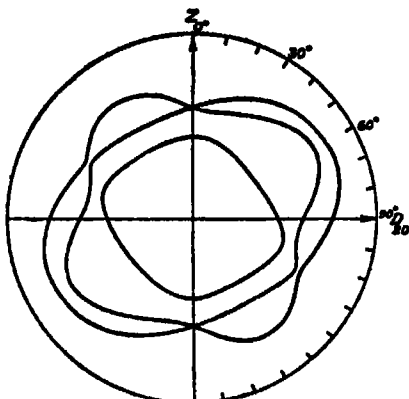


FIG. 4

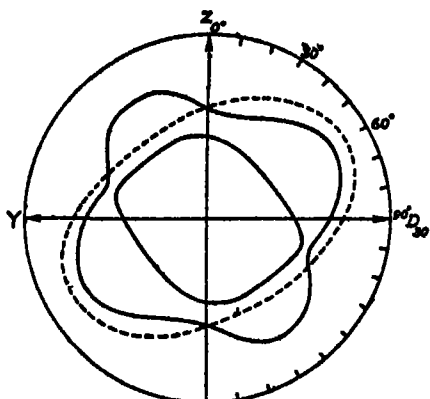


FIG. 5

FIGS 2-5

Schaefer-Bergmann patterns of quartz

In view of the hexagonal symmetry of the pattern shown in Fig. 1, Figs 2 to 5 were drawn to enable the entire three-sheeted surface to be visualised. The sum of the cubes of the three radii vectors of this surface averaged over planes at intervals of 10° , namely 0° , 10° , 20° , 30° , 40° and 50° gave the complete average over the whole solid angle. The general average value of $\frac{1}{C_m}$ in each of these planes was found to be $10^{-18} \times 34.2, 34.8, 34.3, 35.4, 34.3$ and 34.8 , respectively. The general average was thus 34.6×10^{-18} . Using this value, the Debye limiting frequency comes out as 189 cm^{-1} , corresponding to a temperature of 271° T .

3 Superlattice Frequencies of Quartz

The failure of the Debye theory is evident on comparison of the figures in the second and fourth columns in Table II. Since the elastic constants of

quartz are precisely known, it can scarcely be suggested that this failure can be regarded otherwise than as definitely indicating the unjustifiable character of the assumptions on which the Debye theory is based. Mr Saxena's investigation shows that twenty-four out of the twenty-seven degrees of freedom of vibration of the lattice cell are represented by discrete or monochromatic frequencies of vibration. Since the bonds which link the lattice cell together are of the same nature as those that join the atoms within the cell, it must be presumed that even the three remaining degrees of freedom of translation of the lattice cell must also be represented by discrete superlattice frequencies, as explained by Sir C. V. Raman in a paper appearing earlier in this issue. A re-examination of several well-exposed Raman spectra of quartz obtained by Mr T. M. K. Nedungadi and Mr B. D. Saxena at this Institute showed some faint lines with relatively small frequency shifts, which had been previously overlooked. The most prominent of those lines has a frequency shift of 145 cm^{-1} . This line is easily recognizable on all sufficiently well-exposed spectra. Another line with a frequency shift of 69 cm^{-1} which is less intense is very clearly recorded in Mr Nedungadi's best plates and also in some of Mr Saxena's photographs. As they worked with different instruments, there can be no doubt as to the reality of this line. A third line at 95 cm^{-1} is also seen in two of Mr Nedungadi's best pictures and must also be presumed to be real.

As the theory of the superlattice vibrations of quartz has not been worked out in detail, the statistical weight to be attached to these three frequencies in the expression for the specific heat is uncertain. We must evidently expect a series of superlattice frequencies of different orders and of rapidly diminishing statistical weight. A consideration of the higher orders would be necessary for explaining the course of the specific heat curve at the lowest temperatures. As, however, the available data go down only to 25° T , it should be sufficient for our present purpose to consider only the superlattice frequencies of the first order. The two most intense of the recorded lines, namely 145 and 69 cm^{-1} may be assumed to belong to this order. The feebler line at 95 cm^{-1} is a superlattice frequency of either the first or the second order. We shall here assume that it belongs to the second order. Hence, to a sufficient approximation, we need consider only the 145 and 69 lines, and as the former is the more intense, two degrees of freedom may be assigned to it, and the remaining third degree of freedom to the 69 line. The sum of the corresponding Einstein terms in the expression for the specific heat at various temperatures is shown in the fifth column of Table II. It will be seen that the figures are in good agreement with the unexplained residue of the specific heat shown in the second column of the same table at all

temperatures from 31° to 428°T At the two lowest temperatures $25^{\circ}\cdot 8$ and $28^{\circ}\cdot 75$, the agreement is not so good, but the experimental data for these two temperatures are evidently unsatisfactory At high temperatures, the specific heat distinctly tends to be anomalous as in the case of many substances The explanation of the small discrepancy at high temperatures lies outside the scope of the present paper.

In conclusion, the author desires to record his grateful thanks to Professor Sir C V Raman for the kind and valuable interest which he evinced towards this work

4 Summary

From the diffraction patterns obtained by Schæfer and Bergmann with quartz plates vibrating at ultrasonic frequencies, the three sound velocities in various directions in the crystal were evaluated Thence, equating the total number of possible elastic vibrations to thrice the number of lattice cells in the crystal, the Debye limiting frequency was ascertained as 189 cm^{-1} A Debye function for this limiting frequency failed however to agree with the specific heats of quartz after allowance had been made for the contributions of the Einstein terms representing the discrete monochromatic frequencies of vibration of the lattice cell identified by Saxena (1940) The calculated values were much lower than the residual values of the specific heat The failure of the Debye theory is thus unmistakably clear The observed specific heats over the region of temperatures covered by Anderson's recent work (1936) are very satisfactorily explained by including further Einstein terms corresponding to the superlattice frequencies 145 cm^{-1} and 69 cm^{-1} appearing as feeble lines in the Raman spectra of quartz

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THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: ALKALI HALIDES

By DR C S VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1 Introduction

In a recent paper published in these *Proceedings*, the author (1941) has applied the theory of groups to the analysis of the lattice spectrum of rock-salt. The unit cube was assumed to contain four sodium and four chlorine atoms, each group possessing tetrahedral symmetry. The character table for the crystal showed that the twenty-four degrees of freedom of the atoms in the unit cell are distributed among eight modes of triply degenerate vibrations. One of them corresponds to the translations of the cell as a whole. All of them being antisymmetric to the centre of symmetry, are forbidden in the Raman effect. Two of them appear under the symmetry class which is active in the infra-red, while the remaining five are inactive. In the present paper the author proposes to discuss these results in relation to the spectroscopic and specific heat data available for sodium and potassium chloride crystals.

2 Identification of the Lattice Frequencies of Rock-salt

The infra-red spectra—Barnes and Czerny (1931) and Barnes (1932) have carried out detailed investigations of the infra-red absorption spectra of thin plates of several halides and shown that in every case there are at least two, if not three, absorption maxima. One of them is very pronounced and has been identified by them as the principal vibration frequency of the crystal. The others are relatively weak and in cases in which three are observed, one of them almost coincides with the rest-strahlen frequency reported by Schæfer and Matossi (1930). For rock-salt, Barnes and Czerny have given two absorption frequencies at $61.6 \pm 0.3 \mu$ (strong) and 40.5μ (weak). These frequencies have to be identified with the two triply degenerate infra-red active vibrations expected from the group-theoretical analysis of the spectrum.

The Raman Spectra—The Raman spectra of alkali halides do not ordinarily yield any line as was pointed out by Schæfer (1929) and Krishnamurti (1930). Fermi and Rasetti (1931) have subsequently published a remarkable

photograph together with a microphotometric record, of the Raman spectrum of a single crystal of rock-salt taken with 2537 Å radiations of the mercury arc. They have firstly made the observation that the spectrum of rock-salt is very weak, an exposure time of eight hours being required with particularly intense irradiation whereas the strongest Raman line of calcite was recorded in one minute. This extreme feebleness of the spectrum as well as the inability of Schæfer and Krishnamurti to observe the same with 4046 Å U radiations is in agreement with the conclusion arrived at theoretically by the present author. Secondly, these authors have indicated that the spectrum, in the main, consists of bands, one part lying in the close proximity of the exciting line between 0 and 50 cm⁻¹ and the other part lying in the region 160 to 365 cm⁻¹. The region between 50 and 160 cm⁻¹ shows further, a weak continuum. From their reproduced spectrum, several measurable maxima may be easily identified. While many of them are broad, a few are comparatively sharp. The author has measured this spectrum and obtained the following frequency shifts for the middle points of the maxima

TABLE I
The Raman Frequencies of Rock-salt

No	Centre of maxima in cm ⁻¹	Fundamental Frequency in cm ⁻¹	Intensity (Estimate)	Remarks	Assignments
1	40	20	Medium	Broad with Continuum up to 2537 Å U	Lattice Spectrum—4th order
2	85	42	Very weak	Very broad	Lattice Spectrum—3rd order
3	162	81	Weak	do	Lattice Spectrum—2nd order
4	228	114	Very strong	Fairly sharp	Lattice Spectrum—1st order
5	273	136	Medium	do	
6	299	150	Strong	Broad	
7	345	173	do	do	
8	365	183	do	do	

It has been pointed out by Bhagavantam and Venkatarayudu (1939) that the first overtone of every normal mode is active in the Raman effect of especially the crystals, irrespective of whether the fundamental is permitted or forbidden. This would especially be the case for the five inactive frequencies coming under class F_{2u} in the character table for rock-salt. For, the vibrations of the class F_{2g} are Raman active and those of class F_{2u} are similar to the latter except for the fact that they are antisymmetric to the centre of inversion, while those of F_{2g} are symmetric. The sum of the squares of the

characters of these two classes is therefore identical and accordingly, the overtones of the two classes of vibrations are equally probable. As indicated in Table I, the five frequencies, viz., 228, 273, 299, 345 and 365 may be assigned to the first overtones of the vibrations of class F_{2u} . Besides the above, three bands appear with peak frequencies of 40, 85 and 162 cm^{-1} which are broader than the former. These are explained in what follows.

3 Superlattice Frequencies for Rock-salt

In a paper appearing in the present issue of these *Proceedings*, Sir C. V. Raman has indicated that in addition to the lattice vibrations of the smallest unit cell, the crystal possesses superlattice oscillations of several orders, which in favourable cases could be recorded in the Raman spectra of crystals. As the group theoretical method is equally applicable to assemblages of particles as to atoms and molecules symmetrically distributed in space, we shall analyse the superlattice vibrations by considerations similar to those applied to the unit cell itself. It will be remembered that out of the twenty-four degrees of freedom for the sodium and chlorine atoms in the unit cell, three contribute to the translations of the cell as a whole. When we consider similar motions of equivalent atoms in two neighbouring cells, there are two alternatives, viz., that they may move in the same direction (*i.e.*, in phase) or in opposite directions (*i.e.*, opposite in phase). The symmetry of the crystal suggests that eight neighbouring unit cells should be treated at one time, which together have all the elements of symmetry possessed by the unit cell itself. The larger cell thus chosen (or the superlattice cell) is eight-fold in size and contents of the unit cell, and forms a face-centred cubic lattice. The problem of analysing the twenty-four degrees of freedom of translation of this larger unit thus becomes identical with the case of rock-salt which we have already considered. In general, it will be seen that there will be eight triply degenerate vibrations of which one alone is to be attributed to the translations of the unit as a whole. The remaining seven frequencies may be said to form the lattice spectrum of the second order. Taking thirty-two atoms (of Na and Cl) in this greater cell, the group theoretical analysis may be carried out rigorously. Simple considerations however, lead to the ultimate result that each of the seven normal modes of the primary cell, while retaining their nature and frequency nearly the same, become each eight-fold, with the phase of vibration in different cells being the same or opposite as the case may be. In addition, we will get seven discrete frequencies characteristic of the superlattice of the first order. We can now repeat the process to superlattices of higher orders, each successive step yielding seven triply degenerate discrete frequencies together with three degrees of translation as a whole.

The effect of the superlattice vibrations on the normal modes of the smaller unit cell is to multiply each of the latter several-fold. Each line in a crystal thus theoretically represents a group of nearly identical frequencies and should accordingly appear broadened. This is in accordance with the experimental fact observed in several cases that the lattice Raman lines are generally broader than the internal vibrations of molecules or radicals (Venkateswaran, 1938), the latter remain comparatively unaffected by the surroundings due to the much greater strength and stability of the chemical bond involved.

It is common knowledge that the possible frequencies of an atomic group are the closer together, the greater the atomic masses and the smaller the forces between them. We should accordingly expect each group of superlattice vibrations to consist of a fairly narrow band of frequencies. Three Raman bands with their centres at 162, 85 and 40 cm^{-1} appearing in the spectrum of rock-salt (Table I) may therefore be taken as representative of the lattice spectra of the second, third and fourth orders. As in the case of the lattice vibrations of the first order and for the same reason, these frequencies should be taken as the octaves, the fundamentals being respectively 81, 42 and 20 cm^{-1} .

4 The Specific Heat of Rock-salt

It is obvious from the foregoing discussion that in calculating the thermal energy of the crystal, Einstein functions corresponding to the seven triply degenerate frequencies of each order of the lattice spectra should be taken into account, as these spectral lines are essentially discrete in character. As there are four NaCl groups in the unit cell, the contribution to the molar specific heat arising from the lattice vibrations of the first order is

$$\frac{1}{4} \Sigma_1^7 3 R E(\theta_1)$$

where the θ_1 's are given by the frequencies and the temperature of observation. The second order lattice spectrum will yield

$$\frac{1}{4 \times 8} \Sigma_1^7 3 R E(\theta_2),$$

the third,

$$\frac{1}{4 \times 8 \times 8} \Sigma_1^7 3 R E(\theta_3),$$

and so forth. Hence,

$$\begin{aligned} C_p(\text{molar}) = & \frac{1}{4} \Sigma_1^7 3 R E(\theta_1) + \frac{1}{4 \times 8} \Sigma_1^7 3 R E(\theta_2) \\ & + \frac{1}{4 \times 8 \times 8} \Sigma_1^7 3 R E(\theta_3) + \text{etc} \end{aligned}$$

TABLE II
Table of Specific Heats of Rock-salt

Temp in Degrees Absolute	θ_1 VALUES							$\frac{1}{2} \Sigma \theta_1$	θ_2 118	θ_3 54	θ_4 28	θ_5 18	Total C_p (molar) Calcu- lated	C_p^* Experi- mental
	229	354	164	196	214	247	262							
10	008		112	032	0151	004	0012	0431	0014	0216	0110	0020	036	04
20	128		369	149	085	028	018	1943	1248	0917	0173	0024	28	32
25	166		771	374	241	107	074	434	2786	1119	0184	0024	605	58
30	637		1 714	1 081	813	474	369	1 289	4100	1231	0189	0025	99	96
40		0062	1 610	1 900	1 544	1 054	856	2 383	6606	1403	0195	0025	2 10	2 04
50	1 300	257	3 326	2 630	2 260	1 697	1 485	3 50	8356	1481	0198	0025	3 40	3 53
60	2 011	571	3 850	3 218	2 89	2 262	2 077	4 48	9819	1523	0200	0025	4 70	5 2
70	2 609	986	4 258	3 709	3 380	2 840	2 618	5 345	1 031	155	0201	0025	5 70	6 3
80	3 126	1 431	4 782	4 366	4 121	3 673	3 469	6 65	1 109	1568	0202	0025	6 7	7 0
100	3 902	2 30	5 116	4 794	4 591	4 230	4 066	7 588	1 160	1590	0202	0025	7 93	8 28
120	4 434	3 019	5 316	5 071	4 924	4 591	4 479	8 191	1 224	1601	0202	0025	8 948	9 08
140	4 782	3 587	5 467	5 26	5 139	4 899	4 788	8 66	1 254	1608	0203	0025	9 6	9 64
160	5 035	4 03	5 560	5 410	5 290	5 043	5 012	8 98	1 257	1614	0203	0025	10 09	10 05
180	5 208	4 40	5 718	5 500	5 426	5 241	5 173	9 335	1 266	1616	0203	0025	10 42	10 38
200	5 340	4 61	5 885	5 622	5 500	5 442	5 400	9 58	1 276	1620	0204	0026	11 04	10 67
235	5 504	4 954	6	5 856	5 67	5 793	5 774	10 17	1 286	1624	0204	0026	11 54	11 10
300	5 815	5 30	6	6	6	6	6	10 5	1 3125	1643	0205	0027	12	11 60
Maximum														

* These experimental values are those obtained by Nernst and given in *Landolt-Börnstein Tabellen*. They show small variations from those given in the *Handbuch der Experimental Physik* and in the *International Critical Tables* and have therefore to be considered as not of a high order of accuracy.

From the infra-red and Raman spectra we have identified the following seven frequencies for the first order lattice spectrum of rock-salt: 161, 247, 114, 136, 150, 173 and 183 cm^{-1} . These give the $\theta_{1,7}$. As there is at present no spectroscopic method of ascertaining all the seven frequencies belonging to higher orders, it will be assumed, as a first approximation, that they may each be represented by a single frequency for the purpose of the calculation of specific heat. The three Raman frequencies given in Table I, viz., 81, 38 (instead of 42) and 20 cm^{-1} are chosen for θ_2 , θ_3 and θ_4 . In addition, 13 cm^{-1} is chosen as the representative lattice frequency of the fifth order from a perusal of the specific heat data at 20° absolute.

5 Table of Specific Heats for Rock-salt

Assuming the above values of frequencies, Table II exhibiting the specific heats is prepared for rock-salt for the temperature range of $10^\circ - 300^\circ\text{ T}$. The experimental values of specific heat are taken from Landolt and Börnstein Tabellen, and corrected for the work done for the expansion of the crystal by making use of the relation $C_p - C_v = 2.7 \times C_p^2 \times T \times 10^{-5}$ per gram atom, given in the *Handbuch der Experimental Physik*.

6 The Specific Heat of Sylvine

Exhaustive data for the specific heat of potassium chloride are given by Keesom and Clark (1935) from 3° to 17° T and by Southard and Nelson (1933) from 17° to 285° T and are therefore, particularly suitable for the verification of the above expression for the specific heat of crystals. The two infra-red active frequencies recorded for this crystal by Barnes and Czerny are 141 and 212 cm^{-1} corresponding to the absorption maxima at 70.7μ (strong) and, 47μ (weak). Unfortunately the Raman spectrum of sylvine has not been recorded as in the case of rock-salt. However, the remaining frequencies could be deduced from those of the latter on the assumption that

$\nu \approx 2\pi \sqrt{\frac{f}{\mu}}$ Since the force between K^+ and Cl^- is Coulombian, it may be varies as the square of the distance between the atoms, i.e., half the edge of the unit cube. This gives the relation

$$\frac{\nu_{\text{KCl}}}{\nu_{\text{NaCl}}} = \sqrt{\frac{(2.814)^2 \times 13.95}{(3.14)^2 \times 18.61}} = 0.78$$

The corresponding ratio of the infra-red active frequencies being 0.86, it may without serious error be assumed that the average ratio of 0.78 may be used for the purpose of calculation. The frequencies of the lattice spectrum of the first order for KCl thus obtained are $\nu_1 = 141$, $\nu_2 = 212$, $\nu_3 = 89$, $\nu_4 = 107$, $\nu_5 = 116$, $\nu_6 = 135$ and $\nu_7 = 143\text{ cm}^{-1}$. The representative frequencies chosen

TABLE

The Specific

Temp * in Degrees Absolute	θ_1 VALUES							$\frac{1}{2} \Sigma \theta_1$
	202	304	128	153	167	194	205	
2 99								
3 52								
4 01								
4 6								
5 14								
5 72								
6 52								
7 65								
8								
9.23								
10 06			0027					0007

* These temperatures were chosen out of the numerous

TABLE

Temp T° C	202	304	128	153	167	194	205
13 55			0435	0093	0041	0035	
14 73	0013		0776	0196	0093	0079	0011
16 67	0048		166	051	027	0237	0043
21 21	0392		521	221	138	053	034
32 41	456	044	1 88	1 277	932	546	430
39 86	974	168	2 701	1 97	1 641	1 118	932
49 27	1 715	466	3 502	2 815	2 482	1 877	1 660
59 61	2 564	956	4 120	3 531	3 218	2 616	2 414
69 92	3 086	1 493	4 552	3 916	3 772	3 308	2 946
79 11	3 557	1 970	4 819	4 396	4 176	3 626	3 517
89 28	3 957	2 458	5 041	4 686	4 490	4 096	3 902
101 31	4 312	2 954	5 222	4 942	4 770	4 433	4 285
121 41	4 751	3 626	5 442	5 237	5 104	4 845	4 719
141 17	5 036	4 108	5 568	5 405	5 303	5 104	5 011
163 45	5 244	4 536	5 662	5 534	5 467	5 303	5 232
179 76	5 370	4 718	5 717	5 608	5 533	5.425	5 353
201 32	5 483	4 942	5 750	5 676	5 624	5 602	5 476
240 7	5 645	5 219	5 816	5 756	5 724	5 648	5 608
284 7	5 711	5 279	5 826	5 813	5 788	5 732	5 704
Maximum	6	6	6	6	6	6	6

III

Heats of Sylvine

θ_2 80	θ_3 42	θ_4 22	θ_5 14	$\theta_6 + \theta_7$ etc	Total C_v (molar) Calcu- lated	C_v Experi- mental
		00072	00052	00032	0016	00206
	00024	00156	00078	00032	0029	00338
	00074	00256	00101	00032	0046	00470
	00206	00397	00124	00032	0076	00724
	00315	00534	00142	00032	0102	0101
	0057	0067	0016	00032	0143	0145
0009	0108	0085	0017	00032	0219	0191
0041	0204	0106	0019	0003	0373	0368
0058	0238	0111	0020	0003	0430	0460
0169	0391	0129	0021	0003	0710	0620
0291	0449	0138	0022	0003	0907	0840

data available, at regular intervals

III (Contd)

$\frac{1}{2} \Sigma \theta_i$	θ_1 80	θ_2 42	θ_3 22	θ_4 14	C_v Calcu- lated	C_v Ob- served
0151	1248	0773	0164	0023	236	238
0292	1697	0862	0169	0024	304	310
0692	2511	0984	0176	0024	439	438
252	4477	1186	0186	0025	839	842
1 391	8024	1417	0196	0025	2 357	2 358
2 376	9410	1488	0199	0025	3 488	3 52
3 629	1 051	1533	0200	0025	4 856	4 91
4 855	1 122	1563	0201	0025	6 156	6 30
5 768	1 168	1581	0202	0025	7 117	7 33
6 515	1 198	1591	0203	0026	7 895	8 12
7 205	1 222	1599	0203	0026	8 610	8 77
7 729	1 237	161	0204	0026	9 150	9 35
8 431	1 256	161	0204	0026	9 871	10 04
8 884	1 268	161	0205	0026	10 336	10 60
9 245	1 275	162	0205	0026	10 705	10 96
9 431	1 280	162	0205	0026	10 90	11 13
9 638	1 283	162	0205	0026	11 106	11 32
9 854	1 290	162	0205	0026	11 329	11 58
9 963	1 295	162	0205	0026	11 443	11 72
10 5	1 3125	1643	0205	0027	12	

for the second to the fifth orders are respectively 56, 29, 15, and 10 cm^{-1} . It will be noticed that these latter frequencies for the two salts are nearly in the ratio 1 : 0.78. The lattice spectra of orders higher than five are assumed to make their maximum contribution of 0.0032 calories per gm. mol. per degree. $C_p - C_v$ for sylvine is given by $2 C_p^2 \times 10^{-5}$ calories per gram atom.

7 Significance of the Results

The failure of Debye's theory of specific heat in these two cases is well known. Following Born's theory, Blackman (1935), Kellermann (1941) and others have sought to explain this latter as due to a variation of the characteristic temperature of the crystals. Keesom and Clark (1935) have pointed out that this variation of characteristic temperature is anomalous in the case of sylvine at low temperatures. Important deviations from the Debye formulæ in the case of rock-salt have been reported by Clausius, Goldman and Perluck (1934). It will be seen from Tables II and III that the values of specific heats calculated on the basis of the spectroscopic facts agree reasonably well with the observed data for both the crystals throughout the whole range of temperature, which in the case of sylvine nearly approaches the absolute zero. The investigation thus clearly demonstrates that the present approach to the theory of specific heat should replace the earlier ones due to Debye, Born and others.

An examination of the contributions to the thermal energy of each of the orders of the lattice spectra reveals interesting features, giving an insight into the distribution of the thermal energy at various temperatures. The contributions by orders higher than five become significant only at extremely low temperatures (less than 5°K), the contribution of the first two orders of spectra then vanishing. As the temperature is raised to 50° for rock-salt and 40° for sylvine, the fifth and the fourth orders attain their maximum value of 0.0026 and 0.00205 respectively. The contributions of the second and the third orders increase less quickly, becoming the maximum at about 100°K . At room temperature, practically 6/7 of the total energy (*i.e.*, 10.5 out of 12) is due to the lattice vibrations of the first order. The whole of the thermal energy of the crystal can be represented by considering a superlattice cell of edge length $50 \times 10^{-8} \text{ cm}$.

In conclusion the author wishes to thank Sir C. V. Raman for his keen and abiding interest in the work.

Summary

The character table for rock-salt derived from the theory of groups applied to the unit cell containing four atoms of sodium and four atoms of chlorine,

gives eight triply degenerate normal modes of vibrations. One of them corresponds to the translations of the cell as a whole, two are infra-red active and Raman inactive, and five are inactive both in the Raman and the infra-red. The overtones of the latter five modes should however, appear in the Raman effect. This analysis of the vibration spectrum of the rock-salt structure gives a complete explanation of the infra-red absorption spectra of the alkali halides observed by Barnes and the Raman spectrum of rock-salt obtained by Fermi and Rasetti. The two infra-red absorption maxima at 161 and 247 cm^{-1} are taken as the two fundamental frequencies and the five frequencies at 228, 272, 298, 346 and 366 cm^{-1} identified from the Raman spectrum reproduced by Fermi and Rasetti, are assumed to be the first overtones of the remaining five frequencies of the lattice. The latter also shows three broad bands with peak frequencies of 81, 42 and 20 cm^{-1} . These are shown to be the octaves of the superlattice frequencies of the second, third and fourth orders.

A general expression is derived for the thermal energy of cubic crystals of the rock-salt type in terms of the lattice and superlattice frequencies. The expression is evaluated for rock-salt and sylvine for a wide range of temperatures which in the case of sylvine is 3° to 285° absolute. Two of the lattice frequencies for sylvine are given by the infra-red spectrum and the others are deduced from those of rock-salt. The calculated values in either case are in reasonable agreement with experimental data, showing that the thermal energy of crystalline solids is satisfactorily explained on the basis of the ideas indicated in the foregoing paper by Sir C. V. Raman and developed further in the present communication.

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STUDIES IN THE CYCLOHEXANE SERIES

PART V. The Isomeric 1-Carboxy-4-, and 3-Methylcyclohexane-1- α -Benzylacetic Acids

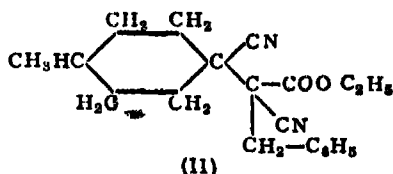
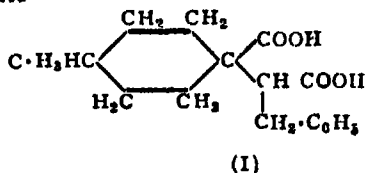
BY R D DESAI, R F HUNTER AND G S SAHARIYA

(From the Department of Chemistry, Muslim University, Aligarh)

Received August 11, 1941

In previous parts of this series¹ we have described the synthesis of the isomeric 1-carboxy-alkylcyclohexane-1-acetic acids, 1-carboxy-3,3-dimethylcyclohexane-1-acetic acid, and 1-carboxy-alkylcyclohexane-1-succinic acids, but no indication was obtained of the isomerism connected with the multiplanar forms of the cyclohexane ring. The reason may be due to the small energy required to change the *boat* form of the cyclohexane ring into the *arm-chair* form. If this energy difference between the two forms is increased by suitable substitution, it may be possible to isolate them as definite entities.

We have, therefore, synthesised 1-carboxy-4-methylcyclohexane-1- α -benzylacetic acid (I) by the hydrolysis of ethyl-1-cyano-4-methylcyclohexane-1- α -benzylcyanoacetate (II) which is readily obtained by the benzylation of ethyl-1-cyano-4-methylcyclohexane-1-cyanoacetate, prepared by the condensation of the cyanohydrin of 4-methylcyclohexanone with ethyl sodio-cyanoacetate. The acid (I) was isolated in two isomeric forms, which were characterised by the preparation of their anhydrides, anilic acids, and imides. A similar pair of isomeric acids was obtained from the benzylation product of the sodio-derivative of ethyl-1-cyano-3-methylcyclohexane-1-cyanoacetate.



The results obtained by us in the present investigation can be interpreted on the assumption of the uniplanar form of the cyclohexane ring. No unequivocal chemical evidence has so far been adduced in favour of the strainless forms of this ring. Qudarat Khuda² claimed to have isolated the four isomeric forms of 1-carboxy-4-methylcyclohexane-1-acetic acid, and argued this as an evidence in favour of the multiplanar forms of the cyclohexane ring. Subsequent investigations, however, by us (*loc cit.*), as well

as Goldschmidt and Gräfinger³ have been unable to substantiate these claims. Moreover, 1-carboxy-4:4-dimethylcyclohexane-1:1-diacetic acid has been shown by us⁴ as well as Roger Adams and Miller⁵ to exist in one form only. Qudarati Khuda and his co-workers⁶ have also described the isolation of 1-carboxy-3-methylcyclohexane-1-acetic acid and 1-carboxy-2-methylcyclohexane-1-acetic acid in four isomeric forms, contradictory to the observations of Desai, Hunter, Khan and Sahariya (*loc cit*), but the repetition of this work by one of us (R D D) according to the details of the authors has shown that the alleged four forms do not exist, and that it is not possible to isolate each of the acid in more than two isomeric forms. Thus the claims of Qudarati Khuda and his co-workers are unconfirmed, and the conclusive chemical evidence in favour of the cyclohexane ring is yet wanting.

Experimental

1-Carboxy-4-methylcyclohexane-1- α -benzyl-acetic acids *Benzylation of Ethyl-1-cyano-4-methylcyclohexane-1-cyanoacetate*—1-Cyano-1-hydroxy-4-methylcyclohexane (32 g) was gradually added to ethyl sodiocyanoacetate (Na = 5.3 g., alcohol = 60 c.c., ethyl cyanoacetate = 28.5 g), and the mixture was allowed to remain at the room temperature for 48 hours. The mixture was kept at the same temperature for further two days after the gradual addition of benzyl chloride (29 g), and then heated on the water-bath under reflux for 24 hours. After the recovery of alcohol, the residue was added to a large quantity of water, and the precipitated viscous mass was extracted with ether, dried, recovered and distilled, giving a fraction b.p. upto 125°/6 mm, a fraction b.p. 125–200°/6 mm, and ethyl-1-cyano-4-methylcyclohexane-1- α -benzylcyanoacetate b.p. 230–234°/6 mm. The first fraction was rejected, while the second fraction (14 g) was rebenzylated in presence of sodium ethoxide (benzyl chloride = 8 g, Na = 1.4 g., absolute alcohol = 15 c.c.), and the product was worked up as already described. The total yield was 30 gm. Some undistillable residue crystallising from alcohol in white, thick plates (m.p. 143°) was left in the Claisen flask, and was identified as 1-cyano-4-methylcyclohexane-1- α -benzyl-acetonitrile as it gave 1-carboxy-4-methylcyclohexane-1- α -benzyl-acetic acid (B) (m.p. 195°) described below [Found C, 80.8; H, 8.0; $C_{17}H_{20}N_2$ requires C, 80.9; H, 7.9 per cent.]

The Dicyano-benzyl-acetic ester was a straw-coloured, viscous liquid which solidified to a glassy mass, and crystallised from dilute alcohol in white plates (m.p. 84–92°) [Found C, 73.9, H, 7.4; $C_{20}H_{24}O_2N_2$ requires C, 74.0; H, 7.4 per cent.]

Hydrolysis of the ester—The ester (25 g.) was kept in contact with concentrated sulphuric acid (50 c.c.) overnight and water (66 c.c.) then added.

The mixture was heated for 24 hours, diluted with water, cooled and extracted with ether. The ethereal extract was shaken with aqueous sodium carbonate (10%), when the alkaline solution was acidified with concentrated hydrochloric acid, a mixture of acids separated. After saturation of the liquid with ammonium sulphate, the acids were extracted with ether, dried and recovered. As the residue did not solidify because of its contamination with the anhydride formed during the hydrolysis, it was heated with dilute caustic soda solution, filtered, and acidified. The cold solution which deposited some solid acid was extracted with ether, dried, and the acids recovered. The crude solid (m p 150–62°) was treated with warm benzene, when a portion of it dissolved leaving a solid (m p 180–82°). This acid (A) crystallised from dilute alcohol in white, lustrous needles (m p 183°) (eff.) [Found C, 70.1, H, 7.5, $C_{17}H_{22}O_4$ requires C, 70.3, H, 7.5 per cent.]

The benzene mother-liquor gave a solid m p 98–106° on evaporation. This was rehydrolysed with concentrated hydrochloric acid for 12 hours, and the acids worked up in the usual manner. Extraction with warm benzene gave a further amount of the sparingly soluble acid (A), while the mother-liquor on concentration gave another isomeric acid (B) (m p 190–92°). It crystallised from dilute alcohol in colourless, thick plates (m p 195°), and depressed to 165° by the acid (A). The amount of this acid was small, but some more of the same acid was obtained from the *dinitrile* which was left in the distillation flask. The ratio of the acid A:B was 10:1 [Found C, 70.2, H, 7.9, $C_{17}H_{22}O_4$ requires C, 70.3, H, 7.5 per cent.]

Derivatives of the Acid (A) (m p 183°) —

The Anhydride prepared by heating the acid in an oil-bath at 165–70° for three hours crystallised from hexane in long, white needles (m p. 115°) [Found C, 75.0, H, 7.4, $C_{17}H_{20}O_3$ requires C, 75.0, H, 7.3 per cent.]

The Anilic acid prepared by mixing the anhydride (0.3 g) and aniline (0.3 g) in benzene solution crystallised from dilute alcohol in needles (m p 165°) [Found C, 73.5; H, 7.4, $C_{23}H_{27}O_3 \cdot N \frac{1}{2} H_2O$ requires C, 73.8; H, 7.5 per cent.]

The Imide obtained by heating the dry ammonium salt of the acid at 180° for three hours crystallised from dilute alcohol in clusters of white needles (m p 181°) [Found C, 74.8, H 7.9; $C_{17}H_{21}O_2 \cdot N$ requires C, 75.1, H, 7.8 per cent.]

The calcium and barium salts of the acid were soluble in water while the lead and copper salts were insoluble.

Derivatives of the Acid (B) (m p. 195°) —

The *Anhydride* obtained by heating the dry acid at 165–70° for three hours crystallised from hexane in needles (m p 109°) (depressed to 93–94° by the anhydride A) [Found C, 74.9, H, 7.5, $C_{17}H_{20}O_3$ requires C, 75.0, H, 7.3 per cent]

The *Anilic acid* crystallised from dilute alcohol in white needles (m p 175°) (depressed to 151° by the anilic acid A) [Found C, 73.4, H, 7.5, $C_{23}H_{27}O_3N \frac{1}{2} H_2O$ requires C, 73.8, H, 7.5 per cent]

1-Carboxy-3-methylcyclohexane-1- α -benzyl acetic acids—Ethyl-1-cyano-3-methylcyclohexane-1-cyanoacetate, prepared from freshly distilled 1-cyano-1-hydroxy-3-methylcyclohexane (20 g) ethyl cyanoacetate (18 g) and sodium ethoxide (3.2 g of sodium and 40 c.c. of absolute alcohol) was kept for 48 hours and treated with benzyl chloride (20 g). The ester was obtained as a viscous oil which was extracted in ether, dried, recovered and distilled, giving a fraction b.p. upto 125°/8 mm, a fraction b.p. 130–200°/8 mm, and ethyl-1-cyano-3-methylcyclohexane-1- α -benzylcyanoacetate, b.p. 237–39°/8 mm, which solidified to a hard, glassy mass. The first fraction was rejected while the second fraction (24 g) was re-treated with benzyl chloride (12 g) in presence of sodium ethoxide (2.3 g of sodium and 30 c.c. of absolute alcohol). The total yield of the *dicyanobenzylacetic ester* was 20 gm. It crystallised from dilute alcohol in clusters of thick plates (m p 95–105°) [Found C, 73.6, H, 7.4; $C_{20}H_{24}O_4N_2$ requires C, 74.0, H, 7.4 per cent]

Hydrolysis of the ester—The ester (20 g) was hydrolysed as usual, and as the crude mixture of acids isolated by ether did not solidify owing to the presence of some anhydride it was heated with 10 per cent NaOH for half an hour, and the acids recovered as usual after acidification with concentrated hydrochloric acid. The crude mixture (m p 60–120°), on trituration with warm benzene left a solid (m p 180–82°), which recrystallised from dilute alcohol in needles (m p 184°) and was identified as *1-carboxy-3-methylcyclohexane-1- α -benzyl-acetic acid (A)* [Found C, 69.8, H, 7.6, $C_{17}H_{22}O_4$ requires C, 70.3, H, 7.5 per cent]

Its calcium and barium salts were soluble in hot as well as cold water, while the lead and copper salts were insoluble. The benzene mother-liquor was concentrated, and some more of the acid (A) was obtained. On further concentration of the mother-liquor, a fraction (m.p. 165–68°) was deposited. It recrystallised from dilute alcohol in white, tiny needles (m p. 178°) (depressed to 165° by the acid A) and was the *isomeric acid (B)*. The proportion of A : B was 10:1. The two isomeric acids were similar in the solubilities of their

lead, copper, calcium and barium salts. [Found C, 70.1, H, 7.8, $C_{17}H_{20}O_4$ requires, C, 70.3, H, 7.5 per cent]

Derivatives of the Acid (A) (m.p. 184°) —

The Anhydride prepared by heating the dry acid at 165–70° for three hours crystallised from hexane in plates (m.p. 102°) [Found C, 74.8, H, 7.6, $C_{17}H_{20}O_3$ requires C, 73.0, H, 7.3 per cent]

The Anilic acid crystallised from dilute alcohol in tiny needles (m.p. 152°). (Found C, 75.3; H, 7.5, $C_{23}H_{27}O_3$ N requires C, 75.6, H, 7.3 per cent)

The Imide crystallised from dilute alcohol in needles m.p. 165–166° [Found C, 74.9, H, 8.0, $C_{17}H_{21}O_2N$ requires C, 75.1, H, 7.8 per cent]

Derivatives of the Acid (B) (m.p. 178°) —

The Anhydride obtained by heating the dry acid at 170° for three hours crystallised from hexane in white needles (m.p. 130°) [Found C, 74.6, H, 7.4, $C_{17}H_{20}O_3$ requires C, 75.0, H, 7.3 per cent]

The Anilic acid crystallised from dilute alcohol in white, lustrous needles (m.p. 170°) [Found C, 75.4, H, 7.4, $C_{23}H_{27}O_3$ N requires C, 75.6, H, 7.3 per cent]

Summary

Benzylation of the sodio-derivative of ethyl-1-cyano-4-methyl-cyclohexane-1-cyanoacetate yields a dicyano ester, which gives a pair of isomeric 1-carboxy-4-methylcyclohexane-1- α -benzylacetic acids on hydrolysis. Similar pair of isomeric 1-carboxy-3-methylcyclohexane-1- α -benzylacetic acids has been also obtained. These results can equally be interpreted on the uniplanar form of the cyclohexane ring.

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RAMAN SPECTRUM OF MERCURIC CHLORIDE IN RELATION TO ITS STRUCTURE

BY K V KRISHNA RAO

(From the Department of Physics, Andhra University, Waltair)

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1 Introduction

THE experimental determination of the relative positions in space of the atoms in a molecule, can now be effected by a variety of methods. Diffraction of X-rays by solids, diffraction of electrons by vapours, measurement of dipole moments, absorption spectra and Raman spectra in different states of aggregation are among the most important ones. A study of the structure of mercuric chloride, from some of the aspects stated above, has been undertaken by many earlier investigators.

Braekken and Scholten¹ concluded, from studies on X-ray diffraction, that HgCl_2 crystallises in the rhombic class with four molecules in the unit cell, the space group being V_h^{16} . According to them, the structure is molecular and the atoms in each molecule are collinear. Braune and Knoke² determined the nuclear distances of HgCl_2 by the electron diffraction method. Greg³ also undertook a detailed study of the structure of mercury halides by the electron diffraction method and concluded that it is not possible to uniquely determine the configuration of the mercuric chloride and bromide owing to the relatively small scattering powers of the atoms attached to the mercury atom. These authors expressed the opinion that their results are, on the whole, in agreement with a linear structure for the molecule. The dipole moment of mercuric chloride, calculated by Bell⁴ from solubility data, is 4×10^{-18} . Curran and Wenzke⁵ determined the same, using dioxane as solvent and found it to be 1.29×10^{-18} . As the value is quite appreciable, the authors conclude that the configuration of mercuric chloride is not linear. On the contrary, Braune and Linke⁶ determined the dielectric constant of HgCl_2 at temperatures between 320°C and 430°C and found the molecular polarisation to be independent of temperature. This shows that the molecule has no dipole moment and has therefore to be linear.

Krishnamurty⁷ studied the Raman spectrum of HgCl_2 in the form of crystalline powder. He recorded two lines 312 (strong) and 381 (weak). As the spectrum resembles those of CO_2 and CS_2 , he suggested a linear model for the HgCl_2 molecule. The presence of the weak line is explained as due

to the oscillation of one of the chlorine atoms against the remaining group (HgCl). This explanation is, however, open to serious objections. He also examined a very concentrated solution of mercuric chloride in CH_3OH . The line is symmetrically broadened and slightly displaced (319). The broadening observed is explained as due to the increased rotational freedom of the molecules in the dissolved state. Braune and Engelbrecht⁸ found that HgCl_2 , dissolved in water, gives a strong line at 320 cm^{-1} and in acetic ester gives a line at 332 cm^{-1} . They also studied the Raman spectrum in the molten and vapour states. Molten HgCl_2 gives a strong and broad line at 314 cm^{-1} and a very weak line at 376 cm^{-1} . In the gaseous state the principal line, according to these authors, shifts to 355 cm^{-1} . The variation of Raman frequencies, as we pass from the liquid or solid state to the gaseous state, is a characteristic of polar molecules. So the obvious conclusion to be drawn from the above result, is that HgCl_2 is polar and hence, a bent molecule.

The existence of strong Raman lines in HgCl_2 is an outstanding evidence that the link in the molecule is covalent. Sidgwick and Powell⁹ collected the experimental evidence as to the stereochemistry of polyvalent atoms and tried to relate it to the simplest expression of electronic structure, the size of the valency groups and the number of shared electrons they contain. They generalised that the structure is always linear when the valency group is less than 8 with a covalency of 2. As HgCl_2 belongs to this category, it should be expected to be linear.

From what has been said in the foregoing paragraphs, it will be seen that evidence, available from different branches of investigation in the matter of the structure of HgCl_2 , is conflicting. In some cases, different authors, working in the same branch, have arrived at different conclusions. It is very important that the structure of HgCl_2 should be definitely established and the discrepancies reconciled.

In the present paper, the author has made a detailed study of the different aspects of the Raman spectrum method. The results are presented and discussed with special reference to the structure of HgCl_2 .

2 Experimental Technique

The following technique is adopted for obtaining a good specimen of the solid suitable for Raman spectrum studies. The substance is contained in a pyrex glass tube and is melted by means of cylindrical electric heater surrounding the tube. The substance is then slowly cooled down to the room temperature by reducing the current in the heater. In this way, a reasonably transparent solid lump is obtained in the glass tube. The tube is cautiously broken and a single transparent crystal of size $1\text{ cm} \times 1\text{ cm} \times 1.5\text{ cm}$ is obtained from the lump. Two of its faces, one for illumination and the other for

observation, are ground and polished. The specimen of a single crystal so prepared is used in the present investigation.

For obtaining the Raman spectrum in the liquid state, a pyrex glass tube of $\frac{3}{4}$ " diameter, flattened at one end and drawn out at the other into the shape of a horn, is used as the container. A cylindrical heater, open at either end, and provided with a window $6\text{ cm} \times 2.5\text{ cm}$ in its body, lengthwise, for the purpose of illumination has been constructed. The Raman tube is supported longitudinally inside the heater by means of two brass discs. A thermometer is inserted and suitable arrangements are made for preventing parasitic light from entering the spectrograph.

To get the polarisation characters of the lines, the horizontal and vertical components are simultaneously photographed interposing a suitably oriented double-image prism in the track of the scattered light. A set of intensity marks is given on the same plate by the method of varying slit-widths. A standard quartz globe tungsten ribbon lamp is used as the source. A steady current of 14.8 amperes is maintained in the lamp by feeding it from a battery of 220 volts. In calculating the polarisation characters, one must take into account several sources of error. The polarisation characters of the Raman lines of CCl_4 are determined with the same arrangement and the correction term necessary to bring the depolarisation factors of the lines 218 cm^{-1} and 312 cm^{-1} to 86%, is calculated. In this manner, it is found that the various errors are corrected for, if the observed value for the instrument employed in the present investigation is reduced to 56% of itself.

For purposes of studying the Raman spectrum in the dissolved state, pure recrystallised sample of the substance is dissolved in methyl alcohol which is purified by distillation over calcium. The concentrated solution, which is of about 30% by weight of HgCl_2 , is filtered through several thicknesses of filter-paper two or three times and finally filtered into the Raman tube. The spectrum is photographed by the usual arrangement for liquids.

A special container, consisting of a thick-walled pyrex tube of diameter 3 cm and length 23 cm, has been used for studying the Raman spectrum of this substance in the vapour state. A few crystals of HgCl_2 are contained in the tube which is sealed off after evacuation. The tube is heated, in the furnace already described, to a temperature of about 300°C and an exposure of about 100 hours has been found necessary for recording the Raman spectrum in the vapour state.

In all cases, the light from a six-inch quartz mercury lamp is focussed on to the container or the substance by means of a large glass condenser and a Fuess glass spectrograph having a high light-gathering power has been used. Wherever necessary, suitable filters have been used in the path of the incident beam to effectively cut off the continuous spectrum in the incident light.

3 Results

The following table gives the Raman shifts in solid HgCl_2 . The numbers in the brackets represent the relative intensities

TABLE I

Exciting line A U	Wavelength of the Raman line A U	Frequency cm^{-1}	Raman shift cm^{-1}
4358	4431 4	22560	378 (0)
"	4418 7	22625	313 (10)
"	4299 9	23251	- 313 (3)
4078	4130 8	24202	314 (2)
4047	4098 8	24391	314 (8)
"	4067 0	24581	124 (2)
"	4062 2	24610	95 (1)
"	4058 5	24633	72 (3)
"	4034 7	24778	- 73 (2)
"	4026 6	24823	-123 (1)
"	3995 9	25019	-314 (2)

$$\Delta \nu = 73, 95, 124, 314, 378$$

The spectrogram is reproduced in Plate XXXV. The lines 73, 95 and 124 are recorded for the first time.

Table II gives the results obtained with the liquid

TABLE II

Exciting wavelength A U	Wavelength of the Raman line A U	Frequency cm^{-1}	Raman shift cm^{-1}
4358	4431 2	22561	377 (1)
"	4423 2	22602	336 } 315 (10)
"	4414 7	22645	293 }
4348	4406 3	22688	307 (1)
4358	4302 8	23234	-296 } -319 (5)
"	4294 3	23280	-342 }
4348	4289 1	23308	-313 (0)
4078	4130 9	24261	315 }
"	4127 0	24224	292 } 304 (2)
4047	4102 4	24369	336 }
"	4096 2	24405	300 } 318 (8)
4078	4027 6	24822	-316 (0)
4047	3997 8	25007	-302 }
"	3992 6	25039	-334 } -318 (2)

$$\Delta \nu = 314, 377$$

The breadth of the strong line is about 40 cm^{-1} . The two edges of the line are measured and the Raman shift is taken as the mean of these two frequencies. A microphotometric record showing the comparative structures of the solid line and the liquid line is reproduced in the Plate.

Table III contains the results obtained in a solution of HgCl_2 in CH_3OH and in the HgCl_2 vapour

TABLE III

State	Exciting wavelength A U	Wavelength of the Raman line A U	Frequency cm^{-1}	Raman shift cm^{-1}
Solution	4358	4420 1	22618	320
Vapour	4047	4098 0	24395	310

The frequencies obtained by the author are in agreement with those obtained by earlier investigators except in the case of gas. This result is very significant and is discussed later on.

The polarisation values obtained in the liquid state are as follows 314 (51%), -314 (52%) and 376 (P). The above values are corrected for the various errors as mentioned before. As the second line is very weak it is not possible to actually measure the depolarisation factor, but it is found that it is also polarised.

4 Discussion of Results in Relation to Structure

As has already been mentioned there are two possibilities to be considered namely (i) a linear configuration and (ii) a bent one for the mercuric chloride molecule. The point group of the symmetrical molecule is $D_{\infty h}$ and such a structure should give rise to one polarised Raman line. The bent structure comes under the point group C_{2v} and should accordingly give rise to three Raman lines, two of which should be well polarised and the third one, usually of the highest frequency should be depolarised to the limit. As mercuric chloride gives rise to two lines, it is difficult to decide between these two alternatives by studying the number of Raman lines only. Nevertheless, it can be argued that since the line 314 is very strong, the other two lines, which should be present if HgCl_2 is a bent molecule, should be sufficiently intense compared to the intensity of the strong line 312. The extreme weakness of one line 318 and the non-existence of the other line suggest that it is not a bent molecule. This view is confirmed by the following considerations.

In the case of polar molecules such as SO_2 , HCl , etc., there are large variations in the frequencies in different states of aggregation. On the other hand, in the case of HgCl_2 , there are practically no variations. The early results of Braune and Engelbrecht show a large variation in liquid and gaseous states, the frequency in the liquid state being 314 and that in the gaseous state 356. They accordingly concluded that HgCl_2 is a polar molecule and

hence a bent one. Contrary to these observations, the results of the present investigation show the frequency, which is 314 in the solid and the liquid states, is 310 in the gaseous state. The very small variation of 4 wave numbers is not of much significance. The two frequencies are practically identical in the solid and the liquid states. In the solution there is a very small shift to the longer wavelength side. So we can conclude that there are no marked variations of frequencies in different states. Hence HgCl_2 should be non-polar and therefore, a linear molecule.

There is yet another line of reasoning which shows that it is a linear molecule. In the case of the bent molecule, we shall designate the parallel symmetrical vibration by ν_1 , the parallel deformation vibration by ν_2 and the asymmetric perpendicular vibration by ν_3 . ν_1 and ν_2 should be polarised and ν_3 depolarised. Accordingly, SO_2 gives three lines at 526, 1146 and 1340. 1340 has been found to be depolarised to the limit. In the present case the strong line 314 may be identified with ν_1 . ν_3 should be on the longer wavelength side of ν_1 and should be depolarised. If we identify 378 with ν_3 , it should be depolarised in case the molecule is bent. But the results obtained in this investigation show that 378 is polarised. Hence, the polarisation values do not fit in with a bent model. The considerable depolarisation of the total symmetric line is due to the broadening of the line which may presumably be identified with rotational scattering. The weak line in HgCl_2 is polarised as in the case of 798 in CS_2 and 1285 in CO_2 . Hence this may be identified with the overtone of the forbidden frequency as in the case of CO_2 and CS_2 . Raman effect data of HgCl_2 strongly support the view that the molecule is linear.

5 Some Special Features

Good Raman spectra of the solid and the liquid are obtained in the present investigation. The plates are run through a Moll microphotometer and the relative intensities of the Stokes and anti-Stokes components are obtained in the usual way with the help of intensity marks recorded on each plate. Results are given in Table IV.

TABLE IV

State	Temp °C	Frequency	$\frac{I_s}{I_{A.S}}$ Obs	$\frac{I_s}{I_{A.S}}$ Calc
Solid	29	314	3.8	4.0
Liquid	280	314	1.6	2.0

It is evident from the above table that the observed value is in agreement with the value calculated in the case of the solid. The agreement between the

observed and the calculated values is not very satisfactory in the liquid presumably because the liquid is slightly yellowish and the results are not corrected for absorption

The principal line is considerably broadened in the liquid state and has acquired an unsymmetrical distribution of intensity. A satisfactory explanation of this interesting phenomenon is at present difficult to furnish. It may be suggested that, as the temperature is very high, a good proportion of molecules, excited to different vibrational states, may be expected to be present. The vibrational frequencies, arising from such molecules, may be expected to give rise to a broad band of a composite character. Other issues such as the increased freedom of rotation at high temperatures, may also have to be taken into account. This is suggested by the fact that the band, as a whole, exhibits considerable depolarisation. It may be added here that the line, observed in the crystal, is quite sharp as may be expected.

In the Raman spectrum of the solid, three low frequency lines have been recorded here for the first time. These three lines at 73, 95 and 124 cm^{-1} are to be explained as due to lattice oscillations. From the crystal structure, it is clear that we should expect a number of lines in this region because there are four molecules per unit cell. A detailed correlation of the crystal structure with the observed lattice spectrum is not attempted here. The large intensity of the lattice lines is, however, in accordance with the proposed linear structure and the consequent marked optical anisotropy of the molecule. These three lines may provisionally be ascribed to modes of oscillation in which the molecule, as a whole, tilts about various axes. Such an assignment receives some support from the fact that these lines do not persist in the liquid state. It may, however, be remarked here that Spomer and Teller¹⁰ have recently indicated that the frequency at 70, as obtained from a study of the electronic spectra, may be ascribed to the transverse vibration of the HgCl_2 molecule.

The three lattice lines, which appear in the Raman spectrum of solid HgCl_2 , are absent in the liquid state. This is natural because the lattice lines are characteristic of only the solid state. The Raman spectrum of the liquid exhibits, besides the vibrational Raman lines, unresolved wing in the neighbourhood of the Rayleigh line. The distribution of intensity in the wing is also studied in the present investigation. λ 4358 Å U is selected as the exciting line and the results are given in Table V.

TABLE V

$\Delta \nu$	9	18	27	36	45	54	63	72	81	90	99	108	117	123
I	1318	224	170	132	120	96	87	79	63	60	44	37	29	25

It may be noted that the wing starts with a maximum intensity very near the Rayleigh line and gradually diminishes till it becomes negligible at a distance of about 100 cm^{-1} . Thus the wing in liquid HgCl_2 possesses all the characters that are typical of the wing usually obtained in common liquids.

6 Summary

In this paper an attempt is made to gather as much evidence as possible from different aspects of the Raman spectrum method for the purpose of determining the structure of HgCl_2 .

Raman spectra in the solid, liquid, gaseous and dissolved states are obtained. The solid gives lines at $\Delta\nu$ 73, 95, 124, 314, 378 cm^{-1} . The liquid gives lines at $\Delta\nu$ 314, 377 and exhibits a prominent wing alongside the Rayleigh lines. The three low frequency lines, obtained in the solid state, have been observed for the first time and are explained as due to the lattice oscillations. The principal Raman line $\Delta\nu$ 314 cm^{-1} is found to occur in the same position in the gaseous and the dissolved states also. The constancy of the Raman frequency in all the states of aggregation, is a characteristic of non-polar molecules. Hence it is concluded that HgCl_2 should be non-polar and therefore, a linear molecule.

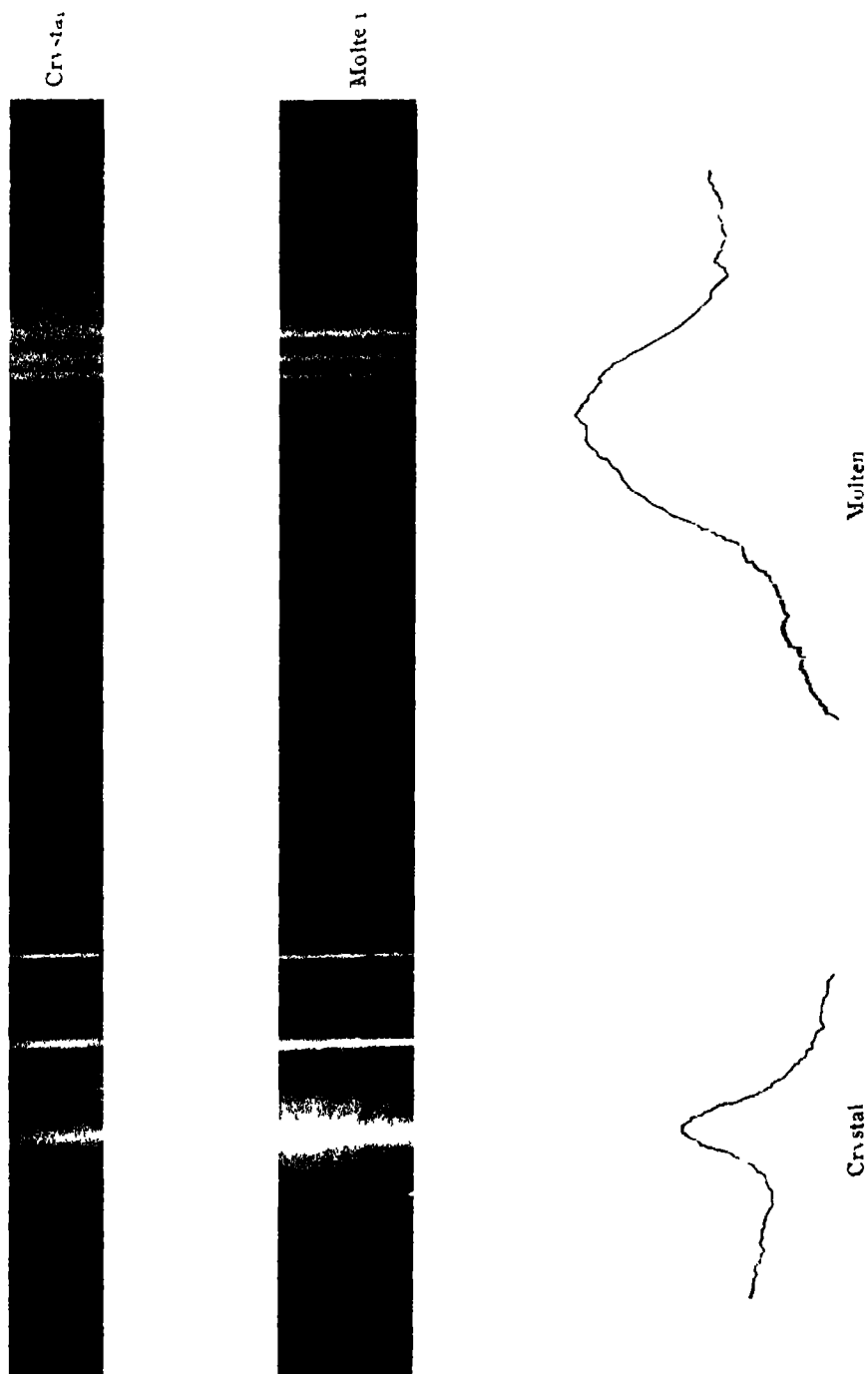
A study of the polarisation characters of the Raman lines in the liquid state reveals that both the Raman lines are polarised. The occurrence of the two lines and their polarisation characters are explained on the basis of a linear structure. The strong line 314 cm^{-1} is attributed to the total symmetric oscillation and 377 cm^{-1} is explained as the overtone of the forbidden frequency.

Incidentally, other prominent features of the Raman spectrum of HgCl_2 , such as the breadth characters of the lines, etc., at different temperatures are noted and dealt with.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam for the keen interest he has shown during the progress of this investigation.

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Raman Spectra of Mercuric Chloride

EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part I. Crystals

BY K. VENKATESWARLU

(From the Department of Physics, Andhra University, Waltair)

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1. Introduction

As early as 1928, Krishnan¹ pointed out that in the Raman spectrum of liquid CCl_4 , the Stokes lines become weaker and the anti-Stokes lines stronger with increase of temperature. Later, Ananthakrishnan² studied the Raman spectrum of liquid CCl_4 over an interval of temperature extending from 25° to 200°C and showed that the integrated intensities of the Stokes lines in CCl_4 do not increase with increasing temperatures.

Birckwedde and Peters³ investigated the Raman spectrum of crystalline quartz between 180°C and 550°C and concluded that the Stokes lines become weaker at higher temperatures. Landsberg and Mandelstamm⁴ reinvestigated the case of quartz and observed that the intensity of the Stokes line at 465 cm^{-1} increased in the ratio 1 : 1.29 when the temperature was raised from 295°K to 810°K .

Recently Ornstein and Went⁵ studied the influence of temperature on the Raman lines of crystalline quartz and calcite over a range extending from 90°K to about 420°K . Some of the important conclusions derived from their experimental investigations are (i) the ratios of intensities of the Stokes and the anti-Stokes lines are in conformity with the theoretically calculated values, (ii) the absolute intensities of the Stokes lines showed marked decrease with rise of temperature; and (iii) the observed decrease in intensity is more pronounced for the lower frequencies.

From the above survey of the experimental work carried out so far in this line of investigation, it is clear that the results obtained in the case of liquids are very meagre and qualitative and that the results obtained in crystals by different authors are at variance with one another. In view of the above facts, it is considered desirable to take up a detailed investigation of the influence of temperature on the intensities of Raman lines both in solids and

liquids Some of the results obtained in the case of a few typical crystals are presented in this paper

2 *Experimental Arrangements*

Light from a 6-inch quartz mercury arc lamp is condensed by means of an 8-inch glass condenser on to one face of the crystal and the scattered light emerging out of one of the other faces of the crystal is focussed on the slit of a two-prism glass spectrograph of high light-gathering power In the case of quartz a cut and polished one-inch cube has been used and the other two crystals, sodium nitrate and mercuric chloride, are grown and polished in this laboratory With suitable precautions, intense and clear spectrograms showing the Stokes and anti-Stokes lines have been obtained

A specially constructed electric heater was made to surround the crystal A mount of oxidised copper foil, prepared carefully so as to give a uniform dull-black surface, is used for mounting the crystal A thermometer kept in contact with the crystal indicated the temperature within an accuracy of $\pm 5^{\circ}\text{C}$ With such an arrangement, the Raman spectra of each crystal at different temperatures have been obtained side by side under exactly identical conditions Great care has been taken to see that the time of exposure and the intensity of the source are kept constant while obtaining the Raman spectra of the same crystal at different temperatures

A set of intensity marks is recorded on each plate by the method of varying slit-widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source The plates are run through a Moll Microphotometer and the densities of the various lines are obtained The density-log -intensity curves are drawn for each wavelength at which the various Raman lines that are to be compared with each other appear The intensity of any line as a fraction of the standard radiation having the same wavelength as the line itself is read from the above curves and the intensities of the Stokes and the anti-Stokes lines are computed from a knowledge of the energy distribution in the radiation emitted by the lamp. Since the crystals are perfectly colourless and not very large, no correction need be made on the score of absorption

As the lines chosen for investigation in the various crystals do not show any appreciable variation in their breadth characters with change of temperature, within the range employed, only the peak intensities are noted and compared.

3 *Results*

Tables I, II and III contain the results relating to the effect of temperature on the intensities of Stokes lines in crystalline quartz, sodium nitrate

and mercuric chloride respectively. The results in column 4 of each of these tables are calculated with the help of relation (1) given in the next section and contained in Placzek's theory

TABLE I

Quartz

$\Delta \nu$	Temp	$\frac{I_T}{I_{308}}$ Obs	$\frac{I_T}{I_{308}}$ Calc	Quotient
465 cm ⁻¹	308° K	1 00	1 00	1 00
	373	0 78	1 07	1 37
	473	0 64	1 17	1 83

TABLE II

Sodium Nitrate

$\Delta \nu$	Temp	$\frac{I_T}{I_{308}}$ Obs	$\frac{I_T}{I_{308}}$ Calc	Quotient
1065 cm ⁻¹	308° K	1 00	1 00	1 00
	378	0 81	1 02	1 26
	423	0 68	1 03	1 51
	493	0 58	1 05	1 81

TABLE III

Mercuric Chloride

$\Delta \nu$	Temp	$\frac{I_T}{I_{308}}$ Obs	$\frac{I_T}{I_{308}}$ Calc	Quotient
315 cm ⁻¹	308° K	1 00	1 00	1 00
	373	0 83	1 09	1 31
	423	0 73	1 17	1 60

Tables IV and V contain results relating to the effect of temperature on the anti-Stokes Raman lines. The results contained in column 4 of each of these tables are calculated with the help of relation (2).

TABLE IV
Quartz

$\Delta \nu$	Temp	$\frac{I_T}{I_{308}}$ Obs	$\frac{I_T}{I_{308}}$ Calc	Quotient
-465 cm^{-1}	308° K	1 00	1 00	1 00
	373	1 25	1 61	1 29
	473	1 52	2 46	1 62

TABLE V
Mercuric Chloride

$\Delta \nu$	Temp	$\frac{I_T}{I_{308}}$ Obs	$\frac{I_T}{I_{308}}$ Calc	Quotient
-315 cm^{-1}	308° K	1 00	1 00	1 00
	373	1 22	1 40	1 15
	423	1 35	1 73	1 28

Tables VI and VII contain results relating to the effect of temperature on the ratio of intensities of the Stokes and the anti-Stokes Raman lines in quartz and mercuric chloride

TABLE VI
Quartz

$\Delta \nu$	Temp	$\frac{h\nu_i}{e^{kT}}$	$\left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^4 \frac{h\nu_i}{e^{kT}}$	$\frac{I_S}{I_{A,S}}$ Obs
465 cm^{-1}	308° K	8 72	7 42	7 68
	378	5 84	4 97	4 79
	473	4 10	3 48	3 25

TABLE VII
Mercuric Chloride

$\Delta \nu$	Temp	$\frac{h\nu_i}{e^{kT}}$	$\left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^4 \frac{h\nu_i}{e^{kT}}$	$\frac{I_S}{I_{A,S}}$ Obs.
315 cm^{-1}	308° K	4 34	3 89	4 12
	373	3.36	3 01	2.80
	423	2.91	2.61	2.25

4 Discussion of Results

The aggregate average intensity per molecule of the Stokes and the anti-Stokes lines has been obtained by Placzek and his results are given in (1) and (2) respectively

$$I(\nu - \nu_j) \propto (\nu - \nu_j)^4 \frac{1}{1 - e^{-\frac{h\nu_j}{kT}}} \quad (1)$$

$$I(\nu + \nu_j) \propto (\nu + \nu_j)^4 \frac{1}{e^{\frac{h\nu_j}{kT}} - 1} \quad (2)$$

From (1) and (2), the ratio of the intensities of the Stokes and the anti-Stokes lines is obtained as in (3).

$$\frac{I(\nu - \nu_j)}{I(\nu + \nu_j)} = \left(\frac{\nu - \nu_j}{\nu + \nu_j} \right)^4 e^{\frac{h\nu_j}{kT}} \quad (3)$$

From the results given in Tables I, II and III it is obvious that the intensity of the Stokes lines, in all the three cases studied, decreases with rise in temperature. This is contrary to what is indicated by equation (1). The discrepancy between the theory and experiment both in magnitude and direction is clearly shown in Fig. 1 (a) for the case of quartz. Results contained in Tables IV and V show that the intensity of the anti-Stokes lines increases with rise of temperature as may be expected. It must, however, be remarked that the rate at which the intensity increases is not in conformity with that contained in the expression (2) and this discrepancy is illustrated graphically in Fig. 1 (b) for the case of quartz. The results given in Tables VI and VII on the other hand, show convincingly that, in spite of the sharp disagreement between experiment and theory that has been noticed in the matter of the individual intensities of the Stokes and the anti-Stokes lines, their ratio as observed at different temperatures is in conformity with the theory.

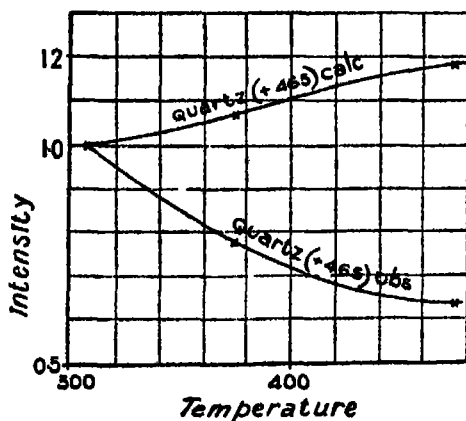


FIG. 1 (a)

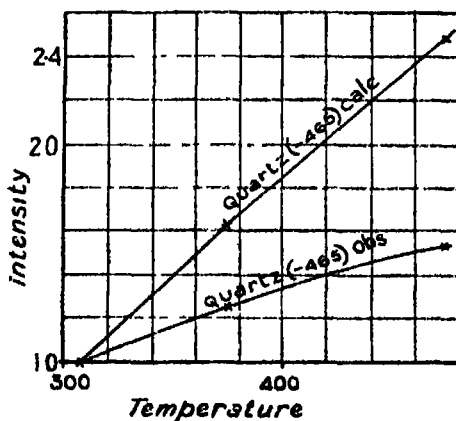


FIG. 1 (b)

It is the main purpose of this paper to draw attention to a failure of the existing theory in respect of the temperature dependence of the intensity of the vibrational Raman lines. The failure appears to be common to the lattice as well as the internal oscillations in crystals. These investigations will also be extended to liquids in due course. The weak point of the theory is in the assumption that molecules in the higher vibrational states, on account of the larger amplitudes involved, give rise to larger scattering moments. This point will be examined and discussed more fully after obtaining data in some typical liquids as well.

5 Summary

The dependence of intensity on temperature of the Raman lines, 465 in crystalline quartz, 315 in mercuric chloride, and 1065 in a sodium nitrate crystal, has been experimentally studied. Sharp disagreements with the existing theories have been noticed in the matter of the individual intensities of the Stokes and the anti-Stokes lines at different temperatures. The experimentally observed ratio of the intensity of the Stokes line to that of the corresponding anti-Stokes line at different temperatures conforms closely to what may be expected on the basis of the existing theories.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam under whose guidance this investigation has been taken up.

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PHYSICO-CHEMICAL STUDIES WITH AQUEOUS FLUORIDE SOLUTIONS

Part I. The Decomposition and Discharge Potentials of Some Fluorides in Aqueous Solution

BY HIRALAL SHRIVASTAVA

(From the Department of Chemistry, College of Science, Nagpur)

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It is well known that fluorides of metals differ noticeably from the corresponding other halides and present several points of considerable interest. A survey of the literature on the subject reveals that in regard to the physico-chemical properties of fluorides there is still, in general, a paucity of information. A systematic detailed investigation of the important properties of aqueous fluoride solutions has been undertaken by the author, and the present paper contains the results of a study of the decomposition potentials and the discharge potentials of some aqueous fluoride solutions at various concentrations with polished platinum electrodes at 25° C. Quite recently, Crockford and Loftin¹ have studied the behaviour of aqueous solutions of hydrofluoric acid and certain alkali fluorides on electrolysis at 0° and 25° C with stepwise increase of applied voltage across rotating, smooth platinum electrodes. From the results obtained they came to the conclusion that electrolytes of the type of hydrofluoric acid and the alkali fluorides have no true decomposition potential in aqueous solution. It appeared to the author that a more detailed study of the problem might lead to a better understanding of it; the present investigation was accordingly undertaken.

Experimental

Preparation of Materials—All apparatus such as containing vessels, beakers, funnels, pipettes, measuring flasks, titration flasks, stirrers, etc., that were to come in contact with hydrofluoric acid or a fluoride solution, were coated with paraffin wax and calibrated thereafter whenever necessary. A platinum basin was used for the preparation of the fluorides.

All the fluorides were prepared in a pure condition in this laboratory except ammonium fluoride, potassium hydrogen fluoride and hydrofluoric acid which were Merck's guaranteed reagents. The methods given in Mellor's

A Comprehensive Treatise on Inorganic and Theoretical Chemistry were followed

The alkali fluorides (LiF , NaF , KF) were prepared from the corresponding acid fluorides by thermal decomposition (Guntz's method⁹) Lithium hydrogen fluoride and sodium hydrogen fluoride were prepared, starting from lithium carbonate and sodium hydroxide respectively, and treating them with hydrofluoric acid

Cadmium fluoride was obtained by the action of hydrofluoric acid in slight excess on cadmium carbonate The mass was evaporated to dryness and then dried completely in an air-oven

Antimony fluoride was prepared by dissolving the trioxide in excess of hydrofluoric acid and evaporating the solution very slowly on a water-bath till crystals began to appear On cooling, large colourless plates separated out (Berzelius, Guntz, Flückiger¹⁰) These were removed and dried between folds of filter-paper, weighed and dissolved in a known volume of water Further drying was found unnecessary, in fact, the crystals were found to decompose on drying over sulphuric acid and then did not dissolve completely in water Analysis corresponds with the composition SbF_3

Silver fluoride was prepared by dissolving freshly precipitated silver carbonate in hydrofluoric acid and filtering off any residue The resulting clear filtrate was found to give a brown or black, sparingly soluble, hard mass on being evaporated to dryness Hence the clear colourless solution itself was diluted as required and kept in darkness in bottles lined from inside with paraffin wax and protected from the action of light by covering from outside with opaque, black, glazed paper The operations in the preparation of silver fluoride were carried out in darkness During a determination also, the solution was kept screened from light. Analysis showed the presence of free hydrofluoric acid to the extent of one mole of the acid for every two moles of silver fluoride The solutions of silver fluoride were found to decompose on keeping, so the analysis and measurements were made soon after the solutions were prepared

The fluoride solutions, except that of silver fluoride, were prepared by dissolving weighed quantities of the fluorides in the requisite amount of conductivity water; exact normalities were determined in all cases by titration with a 0.02 N solution of thorium nitrate using Willard and Winter's method² for the estimation of fluoride as modified by Armstrong³ The thorium nitrate solution was standardised against a 0.02 N solution of Merck's *pro-analysis* hydrofluoric acid; the latter was prepared by dilution from a more concentrated solution, which was standardised against a decinormal solution

of potassium hydroxide using phenolphthalein as indicator. The normality of the diluted acid solution was checked by iodometric method.

Experimental Procedure and Other Details—Decomposition potentials have, in the past, been measured in two ways—one, the direct method, and the other the commutator method. There has been much controversy regarding the correctness of the one or the other method, as the results obtained by the two methods are not in very close agreement. It has been definitely shown by Ferguson and Van Zyl,⁴ and by Knobel,⁵ however, that the direct method is the more correct method; this method has been employed in the present investigation.

An electrically controlled water thermostat regulated at $25^{\circ} \pm 0.1^{\circ} \text{C}$ was used. The electrolytic cell consisted of a 400 c.c. beaker. The electrodes consisted of two polished platinum foils, each 3 sq. cm. in area, and kept 5 cm. apart. The electrode stems were sealed into ends of glass tubes filled with mercury for making electrical contact. The glass tubes carrying the electrodes were passed through holes in a thick wooden disc and sealed in position with paraffin wax. Another hole in the disc carried a thermometer for recording the temperature of the fluoride solution. The disc was also pierced for accommodating a stirrer between the electrodes to keep the electrolyte rapidly stirred in order to eliminate concentration polarisation and to prevent the accumulation of gas bubbles on the electrode surface. To attain this end the previous workers¹ rotated the electrodes themselves.

A gradually increasing potential from two storage batteries connected in series was applied to the electrolytic cell until the decomposition point was well nigh passed. At each stage the potential difference set up between the electrodes was measured with an accurately calibrated potentiometer, and the current flowing was measured by means of a milliammeter in conjunction with an accurately calibrated demonstration galvanometer. Variations in current of the order of 0.01 milliamp. or even less could be easily detected, while the potentiometer could easily detect a variation in potential of 0.25 millivolt.

After each run, the electrodes were cleaned in moderately concentrated nitric acid and washed thoroughly with conductivity water. Each of the electrodes was used alternately as cathode and anode in order to compensate for any difference between them; no difference, however, was detected. Usually three to four runs were made for each salt at each concentration, and at least one check run was always made.

The same procedure was adopted in determining the discharge potentials; the standard half-cell used in these measurements was decinormal calomel electrode. In the case of silver fluoride, a salt bridge consisting of saturated

potassium nitrate was used. In other cases the tip of the calomel electrode was kept in contact with the electrode to be measured.

Typical current-voltage curves are shown in Fig. 1. Only a few points have been shown on each curve, but the curves were actually drawn through a large number of points. The curve for sodium fluoride is typical of the alkali fluorides and ammonium fluoride. Curves for LiF , NaF , KF , NH_4F , KHF_2 , SbF_3 have two breaks each, while those for HF , AgF and CdF_2 have only one break each. The first break for KHF_2 is not well marked.

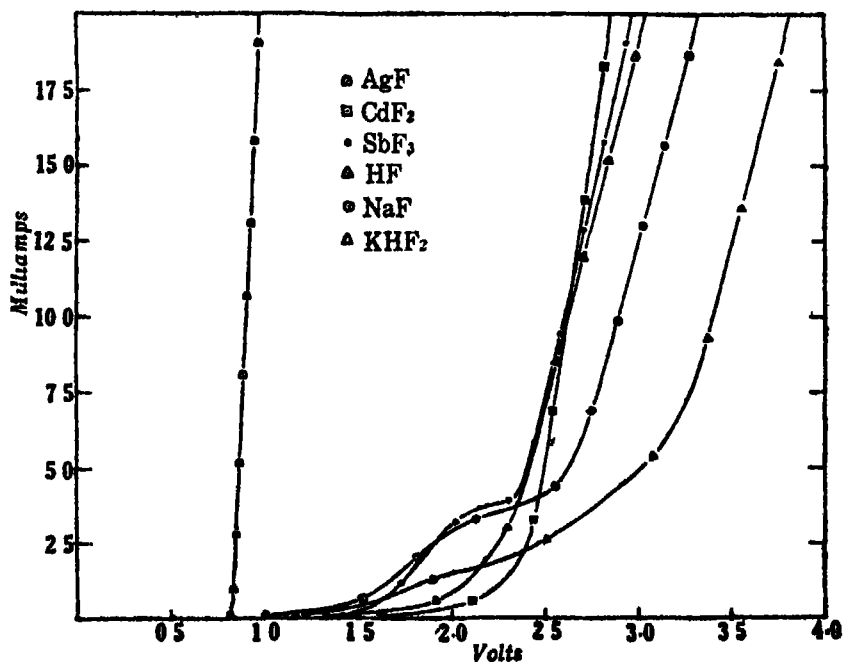


FIG. 1

Current-voltage curves for aqueous solutions of fluorides

Evaluation of Decomposition Potential—In cases where the current-voltage curve exhibits a sharp break, the corresponding potential is quite definite and can be accurately determined. But if the break is not sharp, as is always the case when gaseous products are formed, or where secondary electrode reactions prevail, the value of the corresponding potential is not so definite and depends upon the procedure adopted in determining it. One method is to produce the straight parts of the curve until they intersect; a second procedure is to extrapolate the part of the curve for high current densities back to zero current density; again, a third method is to plot the

logarithm of current density against voltage, and to take the potential corresponding with the intersection of the resulting straight lines as the decomposition potential. All these methods, however, are entirely arbitrary. A change in the scale of plotting a given set of data also changes to some extent the apparent position of the decomposition potential from round curves. The determination of the decomposition potential from round curves cannot, therefore, be made with the same degree of accuracy and certainty as from curves having sharp breaks.

In the present investigation, in determining the potential corresponding to a break in the current-potential curve, the method of producing the straight parts of the curve till they intersect has been followed, because, in the first place, this makes the present data comparable with that of the previous workers¹, secondly, other methods were found to be unreliable in some particular cases.

Results

Groening and Cady⁶ have made a distinction between static decomposition voltage and dynamic decomposition voltage. The former refers to the minimum voltage at which electrolysis just begins, and the electrode processes are practically reversible. The dynamic decomposition voltage is the lowest voltage at which, during electrolysis, the electrode processes are the same as they would be if electrolysis with considerable current density were taking place, and is thus equal to the static decomposition voltage *plus* the cathode and anode overvoltages. It is important to bear this distinction in mind in discussing data on current-voltage relationships.

The potentials for each of the breaks in the current-voltage curves for the fluorides studied are given in Table I, and correspond to dynamic decomposition voltages *plus* the IR drop across the electrodes.

The values for KCl and HCl have been given for comparison. Wherever two breaks occur the potential for the second break has been taken as the true decomposition potential for the fluoride solution concerned except in the case of antimony trifluoride for which the potential for the first break has been taken as the decomposition potential (*vide infra*).

The discharge potentials referred to hydrogen as zero are listed in Table II. In calculating these values the potential of the decinormal calomel electrode at 25° C. has been taken as +0.3376 volt referred to hydrogen electrode as zero. The alkali fluorides and ammonium fluoride may be taken to behave similarly on electrolysis; hence the discharge potentials for ammonium fluoride alone have been determined.

TABLE I

Electrolyte	Normality	Potential in volts at 25° C	
		First break	Second break
LiF	0 056	1 61	2 95
NaF	0 778		2 60
	0 389		2 65
	0 195	1 53 ± 0 02	2 69
	0 078		2 76
KF	0 835		2 72
	0 417		2 75
	0 209	1 50 ± 0 02	2 77
	0 083		2 80
NH ₄ F	0 794		2 65
	0 397		2 62
	0 199	1 62 ± 0 01	2 61
	0 080		2 61
KHF ₂	1 923		3 23
	0 769	1 55 ± 0 05	3 04
	0 240		3 01
SbF ₃	0 948	1 63	2 40
	0 456	1 70	2 51
	0 119	1 86	2 93
HF	2 350	2 20	
	1 175	2 22	
	0 540	2 20	
	0 250	2 20	
	0 121	2 24	
	0 047	2 26	
AgF	1 296	0 73	
(Contains free HF in the proportion 2 AgF-HF)	0 518	0 83	
	0 162	0 90	
CdF ₂	0 420	2 39	
	0 240	2 37	
	0 120	2 38	
KCl ..	1 000	2 22	
HCl ..	1 000	1 31	

TABLE II
Discharge Potentials at 25° C
(Hydrogen Electrode = Zero)

Electrolyte	Normality	Cathode potential		Anode potential
		First break	Second break	
NH ₄ F	0.794	+0 12	−0 50	1 74
KHF ₂	1 923		−0 85	2 12
	0 769	−0 17	−0 93	2 09
	0 240		−1 02	2 00
SbF ₃	0 948	+0 14	−0 17	2 08
	0 456		−0 20	2 03
	0 119		−0 22	2 00
AgF	1 296	+0 74		1 51
(Contains free HF in the proportion 2 AgF-HF)	0 518	+0 72		1 56
	0 162	+0 69		1 58
CdF ₂	0 420	−0 44		1 92
	0 240	−0 45		1 91
	0 120	−0 46		1 90

Discussion

In cases where the current-voltage curve has two breaks, the corresponding current-cathode potential curve also exhibits two breaks, but the current-anode potential curve has only one break in every case. From this it is evident that the occurrence of two breaks is due to two different processes at the cathode.

In cases where the current-voltage curve shows more than one break the question arises as to which of these should be taken to correspond with the decomposition voltage. According to the widely accepted definition of decomposition voltage⁷ as the minimum voltage required for continuous electrolysis (with unattackable electrodes), the potential for the first break ought to be taken as the decomposition potential in every case.

But in the case of the alkali fluorides and ammonium fluoride it appears that the potential for the first break cannot be regarded as the true decomposition potential for these fluoride solutions, because the first break, which occurs at about 1.55 ± 0.05 volts for each of the above fluorides at different concentrations, and which according to the previous workers¹ is independent

of temperature also, corresponds, without doubt, to the primary decomposition of water, *i.e.*, the discharge of H^+ and OH^- ions only at the electrodes. Moreover, there is no break in the current-anode potential curve corresponding with the first break in the current-voltage curve. Further, if the logarithmic method of plotting is used, the first break becomes indistinct and uncertain in every case, while the second break is still very pronounced. The potential for the second break varies with the nature of the metallic ion, and in general, with concentration of a given fluoride solution, but is independent of the rate of stirring provided it is rapid enough to eliminate concentration polarisation and to prevent accumulation of gas bubbles on the electrodes. The previous workers¹ have found that it varies with temperature also. On the basis of these observations the second break may be assumed to be due to the primary electrode process being the discharge of the metallic ions and the fluoride or complex anions existing in solution, and as the products of such a discharge process will readily disappear by reaction with water as soon as they are formed, the above assumption is quite in harmony with the fact that the net electrolytic change is the decomposition of water alone. The potential for the second break may, therefore, be taken as the true decomposition potential for aqueous solutions of the alkali fluorides and ammonium fluoride.

The previous workers¹ are of opinion that as the potential for the normal fluorine electrode is very much higher than the potential required for the decomposition of water, primary decomposition of a fluoride cannot occur in aqueous solution, and the only electrolytic reaction during the entire course of electrolysis is the primary decomposition of water alone, so that for electrolytes of the type of hydrofluoric acid and the alkali fluorides, no true decomposition potential exists in aqueous solution. Such a view, however, seems to be untenable, because in the first place, it fails to account for the occurrence of the second break. One possible explanation might have been that at the second break, either the hydrogen or the oxygen or both, evolved at the electrodes, are in the atomic or excited state. But the difference between the values of potentials for the first and second breaks is far too small to admit of such an explanation. Secondly, the objection against the primary electrode process being the discharge of the metallic ions and the fluoride or complex ions and on the basis of the high potential for the normal fluorine electrode appears to be groundless from analogy with the behaviour of other alkali salts on electrolysis. Le Blanc's values for the decomposition potentials of normal aqueous solutions of the alkali chlorides, bromides and iodides are given in Table III. Undoubtedly, the primary electrode process at these potentials is the discharge of the alkali metal ions and the halide ions. These

values are, however, much lower than those calculated on a theoretical basis from the normal electrode potentials of the different metallic and halogen ions as can be seen from the figures in Table III. The same is true for the alkali sulphates, nitrates, etc.

TABLE III
Decomposition Potential in Volts for Normal Solution

Salt	Le Blanc's experimental values	Theoretically calculated values
LiCl	1.86	4.32
NaCl	1.98	4.08
KCl	1.96	4.28
NaBr	1.58	3.79
KBr	1.61	3.99
NaI	1.12	3.26
KI	1.14	3.46

The difference is obviously due to quick secondary changes on electrode surfaces making themselves felt. A comparison of such figures would be of still less value in the case of fluoride solutions on account of the existence of different kinds of complex ions, the concentration and influence of which are at present not well understood. Evidently, as depolarisation occurs in the presence of complex ions, the salt ions present in fluoride solutions may certainly be discharged at potentials lower than the theoretical value for the elementary ions.

Antimony fluoride also gives two breaks, each of which, however, varies with concentration. When a potential lying between those for the first and second breaks is applied, oxygen is evolved at the anode, although the quantity evolved is very minute; but there is no evidence of gas evolution at the cathode even after continuing the electrolysis for 6 hours. The cathode was, however, fogged, and assumed a shining, brown or black appearance. This was found to be due to the formation of a very thin film of antimony on the cathode. On increasing the potential to that for the second break, oxygen was still evolved at the anode, and antimony separated out in the form of small shining granules at the cathode. The current-cathode potential curve for antimony fluoride also gives two breaks which correspond to the two breaks in the current-voltage curve. The cathode discharge potential for the first break for 0.948 N solution of antimony fluoride (+0.14 volt, cf Table II) corresponds approximately to the potential of the normal antimony electrode (+0.1 volt). The current-anode potential curve gives only one break which corresponds to the first break on the current-voltage curve.

From the above it appears that with antimony fluoride the potential for the first break may be taken as the decomposition potential. The occurrence of two breaks may be due to the separation of antimony in two different forms, and not to a change in the nature of the electrode processes.

Cadmium fluoride and silver fluoride also undergo true decomposition in aqueous solution, cadmium and silver being deposited at the cathode at potentials (*cf* Table II) not considerably different from the normal electrode potentials for these metals (Cd, -0.40 volt, Ag, $+0.7995$ volt). Hence the decomposition potentials determined for these fluoride solutions are the true decomposition potentials. The behaviour of silver fluoride is, however, remarkable in that instead of a gas being evolved at the anode, as is the case with other fluoride solutions, a crystalline deep brown or black deposit is formed on the anode. This may be the reason why the anode discharge potential becomes more positive on dilution in the case of silver fluoride alone. This deposit was found to be almost insoluble in water, but it gave a deep brown solution with concentrated nitric acid. On the addition of a trace of potassium nitrite the solution at once turned colourless but remained very slightly turbid; the turbidity disappeared on heating. It is well known that a black crystalline deposit is formed on the anode when an aqueous solution of silver nitrate or silver sulphate is electrolysed between polished platinum electrodes. This black deposit is a peroxidised product. For details, *cf* Mellor's book.⁸ The nature of the product obtained with silver fluoride is being investigated in detail and will be communicated later. However, this product seems to be fundamentally similar to those obtained with silver nitrate and silver sulphate. A preliminary analysis shows the presence of about 80.59% of silver which, on the assumption that the product is a peroxide, corresponds most closely with the formula Ag_2O_3 .

Reference has already been made to the earlier work by Crockford and Loftin¹ on the electrolysis of aqueous solutions of hydrofluoric acid and the alkali fluorides at 0° and 25°C , between smooth platinum electrodes. These workers also found two breaks in the current-voltage curve for the alkali fluorides. The first break for each fluoride solution had a value lying between 1.62 ± 0.05 volts at both the temperatures. The values for the second breaks at 25°C are listed in Table IV and are the total bath potentials up to this point.

There is a marked discrepancy between the corresponding values of Tables I and IV. This discrepancy, however, on closer examination, seems to be only an apparent one. The previous workers¹ state that in making a determination, approximate curves were obtained, and then accurate data were

TABLE IV
(After Crockford and Loftin)

Electrolyte	Normality	Potential in volts for the second break at 25° C
HF	0.108	1.62
LiF	0.045	2.47
KF	0.100	2.35
	1.000	2.23
NaF	0.100	2.32
	0.755	2.23

obtained by taking a large number of readings at the critical parts of the curves. By this means they have probably determined the potential at which the current just begins to rise abruptly—this being the critical point in the current-voltage curve, hence the values given in Table IV are, in all probability, the static decomposition voltages (*vide supra*) plus the IR drop across the electrodes, whereas the values given in Table I are the dynamic decomposition voltages plus the IR drop. Some ambiguity may, at first sight, arise in regard to the above interpretation of the previous workers' results on account of their statement that the potential up to the second break includes also the overvoltages of the hydrogen and oxygen discharge on smooth platinum in the respective solutions. It may be pointed out, however, that on the probable assumption of the primary electrode process at the second break being the discharge of the salt ions, the above statement is of no significance.

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Summary

The decomposition potentials of HF, LiF, NaF, KF, NH_4F , KHF_2 , AgF, CdF_2 and SbF_3 , and the cathode and anode discharge potentials of NH_4F , KHF_2 , AgF, CdF_2 and SbF_3 , in aqueous solution, have been determined at 25° C at various concentrations using polished platinum electrodes. The current-voltage curves for LiF, NaF, KF, NH_4F and KHF_2 have an initial break at about 1.55 ± 0.05 volts for each concentration, and another break at a higher potential which varies with the nature of the metallic ion,

and also with the concentration of the fluoride solution. The curve for SbF_3 also has two breaks, each of which, however, varies with concentration. The curves for HF , CdF_2 and AgF have only one break each. Of the current-cathode potential and current-anode potential curves obtained, only the current-cathode potential curves for NH_4F , KHF_2 and SbF_3 have two breaks corresponding to the respective breaks in the decomposition current-voltage curves, the other curves have only one break each. These results have been discussed in detail and the inference is drawn that even alkali fluorides may have a true decomposition potential in aqueous solution

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FIXATION OF AROMATIC DOUBLE BONDS

BY S RANGASWAMI AND T R SESHADRI

(From the Departments of Chemistry and Chemical Technology, Andhra University, Waltair)

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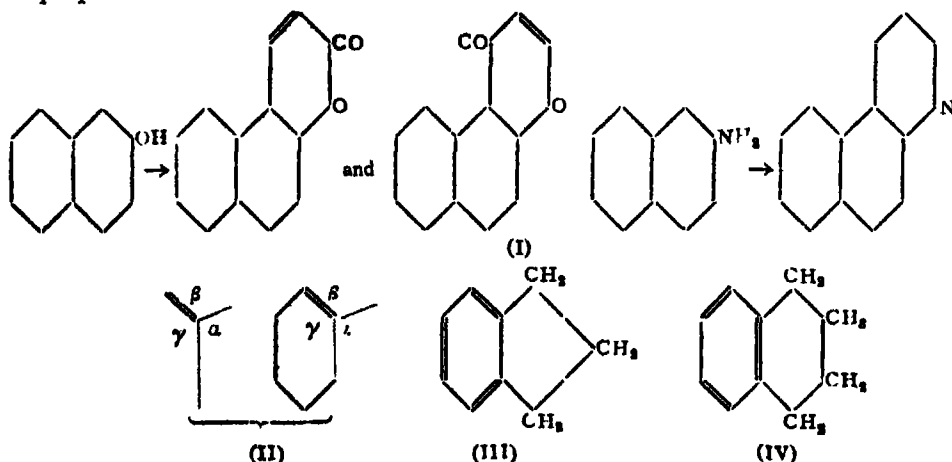
Introduction

THE essential feature of the theory of Kekule relating to the structure of the benzene ring is the existence of oscillating double bonds. Consequently they should have no fixed positions. Based upon this idea the properties and reactions of the compounds of the aromatic series were considered to be satisfactorily explained. When therefore the possibility of the fixation of these bonds in certain favoured positions was announced, it attracted considerable attention and a great deal of work has been done with a view to get clear information of the behaviour of aromatic ring systems.

Work carried out towards the end of the last century and the beginning of this century with reference to derivatives of naphthalene and anthracene indicated the existence of certain select active positions. Fresh rings when formed tended to be of the angular type and not of the linear, as for instance, β -naphthol and β -naphthylamine formed rings (α - and γ -pyrone and pyridine rings) involving the 2, 1 positions and not the 2, 3 as shown in (I). The same phenomenon was noticed in the case of β -substituted anthracenes and anthraquinones. A similar preferential activity was noticed in other reactions such as bromination, nitration, aldehyde formation, etc. But the first to develop a theory on the fixation of aromatic double bonds were Mills and Nixon and the phenomenon is sometimes called the Mills-Nixon effect. If in a doubly bound carbon atom the angle α between the two single bonds is the same as that between the valencies of the carbon atom in methane ($109^{\circ} 5'$) then the angles β and γ which the single bonds make with the plane of the double bond would be each equal to one half of $(360^{\circ} - 109^{\circ} 5')$ or $125^{\circ} 25'$; i.e., β is equal to γ and is greater than α (vide II). In the benzene ring each internal angle is 120° , i.e., γ' is 5° less than γ . If this reduction of 5° in the value of γ' brings about proportionate increases in the values of α' and β' then the difference between these latter (α' and β') will be slightly more than that between α and β . In other words, in the benzene nucleus constituted in accordance with the Kekule formula, the angle which each of the external valencies makes with the intranuclear single bond on

the one side of it is less than that which it makes with the plane of the double bond on the other side, these being roughly in the ratio of 109° 125°

On this hypothesis Mills and Nixon argued that the stable form of a compound in which the benzene ring is fused with a 5-atom ring (internal angle 108°) must be that in which the linking common to the two rings consists of a single bond since such a configuration produces little distortion in the normal directions of the external valencies. Similarly the stable form of a compound in which the benzene ring is fused with a 6-atom ring (internal angle 120°) must be that in which the common link is a double bond. Thus hydrindene should consist of an equilibrium mixture in which the form with the common single bond (III) preponderates, and tetralin of a mixture in which the form with the common double bond (IV) is preponderant.



The effects of fixation are also brought about by fusion with other aromatic rings just as in naphthalene, anthracene, phenanthrene, etc. Carbocyclic rings having five atoms as in fluorene have a similar influence. Fusion with heterocyclic rings such as pyrones, furans, pyridine, etc., have also been studied. It is interesting to record that even such unstable rings as are found in chelate structures have a tendency to bring about fixation of the aromatic double bonds.

The Methods Employed

As already mentioned data obtained from the direction of closing up of fresh rings starting from hydroxy and amino compounds gave valuable indications. Substitution reactions such as bromination and nitration, entry of aldehyde and ketone groups and formation of quinones and acids

in the case of isomeric hydroxy and amino compounds were subsequently utilised. Ingenious methods involving reactivity of methyl groups and of halogens in alternative positions have been employed by Mills and collaborators. Probably the most sensitive of all these methods is the formation of azo-dyes by the action of certain reactive diazonium salts. This has been very largely used by Fieser who has been also responsible for introducing what is known as the blocking technique. If the orientation of the newly entrant groups is dependent upon the presence of a double bond between the carbon atom having a hydroxylic or amino substituent and its neighbour all these methods are capable of locating the position of the double bond. But, as has been frequently realised it is probably more correct to say that there is quantitative difference in reactivity rather than any essential difference in the quality of the neighbouring positions. Fieser's technique of blocking one of the alternative positions with an alkyl group comes in very useful in this connection, since competition between two alternative positions is eliminated (examples are given in detail in subsequent pages). Combining with the blocking technique the very sensitive method of azo-dye formation, he claimed to have in certain cases proved the existence of rigid fixation of aromatic double bonds (naphthalene, anthracene and hydrindene). Another satisfactory method that has been employed to a large extent by Baker in studying the effect of chelate rings was the migration of groups like allyl (Claisen) and acetyl (Fries) from oxygen to carbon. A combination of this procedure along with the blocking method has been employed by Rangaswami and Seshadri in the case of coumarins and chromones with very definite results.

The above chemical methods suffer from certain inherent difficulties since in a number of cases the treatment is not simple. Physical methods have the advantage that they do not disturb the condition of the molecules. The most valuable of these is the determination of dipole moments. The dissociation constants of isomeric acids and phenols have been employed in certain cases and so also the oxidation-reduction potentials of certain quinones. Evidences from Raman spectra, infra-red spectra, absorption and X-ray spectra have also been obtained in a few cases. The lowering of the melting point under water has found application in special cases where chelate ring structures are involved.

For an explanation of the terms 'reactive methyl' and 'reactive halogen' reference may be made to the article on the 'principle of vinylogy' by Fuson.¹ A reactive methyl group is generally identified by its capacity to react with aromatic aldehydes and less frequently with phthalic anhydride

or *p*-nitrosodimethylaniline while a reactive halogen is characterised by its replaceability with hydrogen on treatment with reducing agents like phosphorus and hydriodic acid or acid stannous chloride and with other groups on treatment with bases like alcoholic ammonia, aromatic amines, alkali hydroxides or piperidine

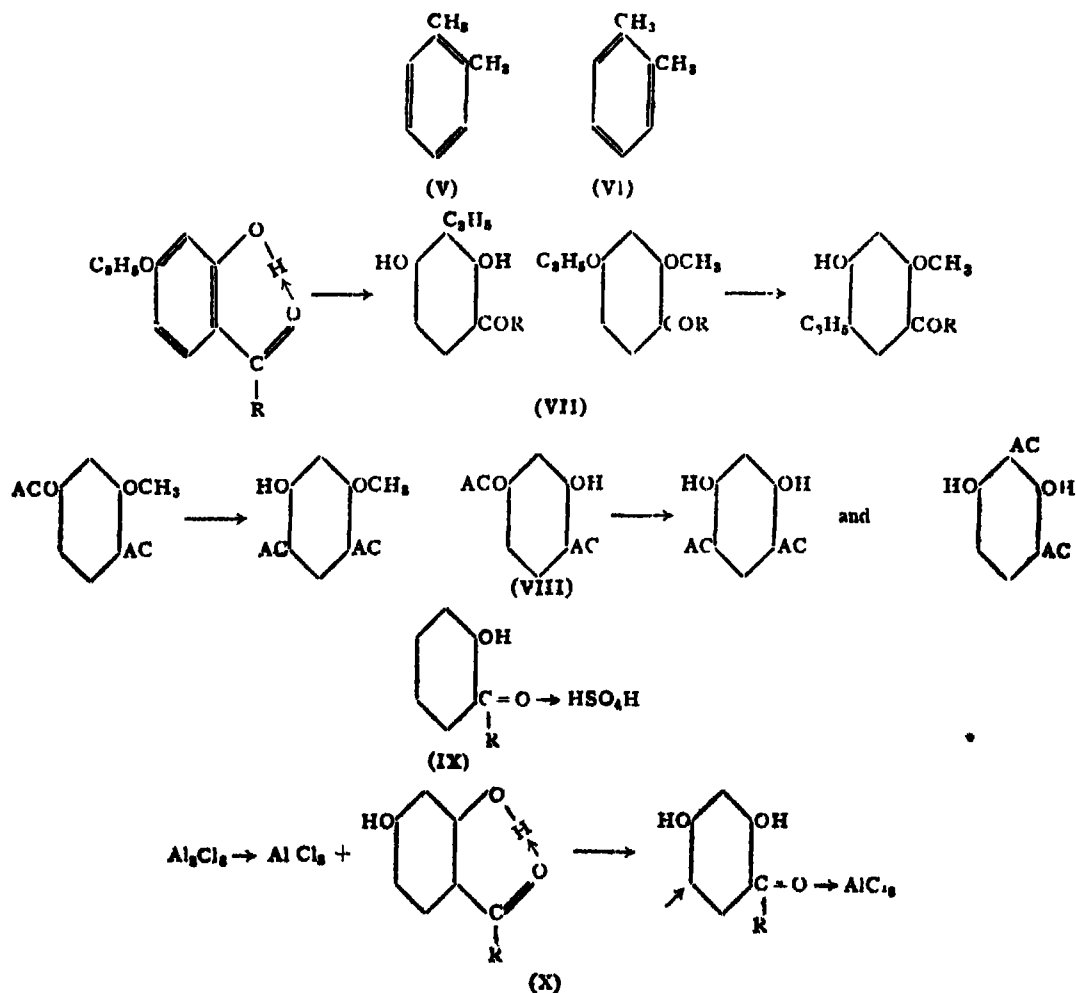
Details of the application of the above methods are given in the following pages where the examples of the important types are dealt with.

Benzene—Considerable amount of work has been done in regard to the structure of this fundamental hydrocarbon molecule using delicate physical methods. All the results indicate that it has a plane symmetrical structure. Of the several chemical experiments made to determine the disposition of single and double bonds in benzene, that of Levine and Cole² deserves special mention here. As the result of ozonisation of *o*-xylene they obtained three products, *viz*, glyoxal, methyl-glyoxal and diacetyl. Neither form of the xylene can yield all the three oxidation products and hence the hydrocarbon should consist of an equilibrium mixture of the two Kekule forms (V) and (VI)

While this gives one side of the picture the work of Baker and others shows that fixation is possible under certain circumstances even in the simple benzene system. Baker and Lothian³ found that 4-O-allylresacetophenone undergoes the Claisen transformation to produce mostly 3-allylresacetophenone though its methyl ether gives 5-allyl-2-O-methyl-resacetophenone under the same conditions (*vide* VII). Baker and Lothian explain these reactions by assuming that in the former case the existence of chelation between the adjacent hydroxyl and acetyl groups fixes one of the nuclear double bonds between the carbon atoms carrying these groups and the other two double bonds are in appropriate positions as shown in (VII). Hence the migration of the allyl group which involves the participation of a double bond is directed to the 3-position. When chelation is prevented as in the methyl ether then migration tends to produce a symmetrically substituted molecule.

Observations which support the above view have been made in connection with other types of reactions as well. Baker⁴ found that though 2-methoxy-4-acetoxy-acetophenone gave 2-4'-diacetyl-5-methoxy-phenol when subjected to the conditions of Fries migration, 4-O-acetylresacetophenone gave a mixture of 2-4- and 4, 6-diacetylresorcinols under the same conditions owing to the operation of the forces of chelation in this case (*vide* VIII). Perkin⁵ found that the methylation of β -resorcylic ester using methyl iodide and methyl alcoholic potash introduced a methyl group into the nuclear

position 3 Using ethyl iodide instead of methyl iodide Robinson and Shah⁶ obtained similar ethylation in the same nuclear position. More recently Rangaswami and Seshadri⁷ have found that under a similar treatment resacetophenone and ω -methoxyresacetophenone produce 3-C-methyl derivatives. Again Shah and others^{8,9} have found that resorcylic ester and resacetophenone undergo the modified Gattermann reaction to give the 3-aldehydes. All these are in conformity with the hypothesis that chelation between the hydroxyl and the carbonyl in the *o*-position does involve a fixed nuclear carbon-carbon double bond. But at the same time the evidences accumulated by a number of workers go to show that this fixation is not very rigid and does not operate under all conditions. For example Baker *et al* (*loc cit.*) themselves conclude from the behaviour of resacetophenone



derivatives that 'fixation by chelation of the Kekule forms in *o*-hydroxy-acetophenones is not rigidly complete' though such fixation occurs 'to a considerable extent'. Similar conclusions can be arrived at from the nature of certain coumarin condensations as reported by Sethna *et al*¹⁰. These authors noted that whereas methyl β -resorcyate and aceto-acetic ester give methyl 4-methyl-5-hydroxycoumarin-6-carboxylate with aluminium chloride as the condensing agent, sulphuric acid produces 4-methyl-6-carbomethoxy-7-hydroxycoumarin; in the first case the γ -position of β -resorcylic ester is the reactive one whereas in the latter it is the free β -position.

The above irregularities are obviously due to the effect of reagents and temperature. Chelation is a special case of the wider phenomenon of hydrogen bond formation. From evidence accumulated in our laboratories chelate bonds seem to be some of the strongest of the type. Still they are not as strong as the ordinary covalent bonds and are possibly ruptured by such reagents as sulphuric acid which have the capacity of co-ordination to a high degree (IX). Regarding the influence of aluminium chloride somewhat contradictory results have been reported. Its behaviour probably varies considerably with the conditions and their effect on the changes represented in (X). It may also be mentioned here that chelation between a hydroxyl and a nitro group in the *o*-position does not seem to involve the participation of a nuclear double bond.

Naphthalene —The structure of naphthalene is probably one of the most thoroughly investigated. A large number of methods have been employed to study the disposition of the nuclear bonds in one half of the molecule and also simultaneously in both the halves. Of the numerous canonical structures only the three represented in (XI), (XII) and (XIII) are important since they are the most stable valence bond structures and make the maximum contribution to the resonance energy of the naphthalene molecule. Among these three since (XII) and (XIII) are equivalent only structures (XI) and (XII) need be considered here. The symmetrical formula (XI) due to Erlenmeyer represents the molecule as being on the whole more aromatic than (XII) and hence would be the more plausible. Kohlrausch¹¹ has reported that the unsymmetrical formula for naphthalene is inconsistent with the Raman and infra-red spectra of the hydrocarbon though the data do not distinguish between the various symmetrical formulæ. Chemical evidence favouring the idea of a double bond between positions 1 and 2 and of a single bond between 2 and 3 is abundant. Thus β -naphthol couples with diazonium salts at C₁ whereas 1-methyl- and 1-allyl-2-naphthols do not couple^{12,13}. Again in the formation of naphthapyrones from β -naphthol it is the 1-position that is involved.^{14,15} β -Naphthol allyl ether rearranges to give 1-allyl-

2-naphthol but 1-allyl-2-naphtholallyl ether does not rearrange (Claisen¹³) Again β -naphthylamine couples at C_1 to form azo-dyes and undergoes the Skraup reaction by ring closure involving position 1 (Marckwald¹⁶) The failure of 2,3-dihydroxynaphthalene to form a quinone (Marckward¹⁷) is definite proof that the HO C C OH system here does not function as a single unit as it would do if the C atoms were connected by a double bond Further evidence for the Erlenmeyer structure can be obtained from the reactivity (*i.e.*, elimination) of the halogen in chloro- and bromonaphthalenes (McLeish and Campbell¹⁸), bromo-aminonaphthalenes (Sandin and Evans¹⁹) and bromonaphthols (Franzen and Straube²⁰) Again Hodgson and Elliot²¹ found evidence for the symmetrical structure in the behaviour of halogeno-naphthylamines during acylation, nitration and hydrochloride formation while Bergmann and Hirschberg²² concluded from the dissociation constants of *o*-chloronaphthoic acids that in naphthalene the single and double bonds have a fixed disposition as depicted by Erlenmeyer and do not undergo any rearrangement

Strictly speaking all the above chemical evidence proves the disposition of bonds only in one part of the molecule They do not necessarily indicate a symmetrical structure for the entire molecule and can be explained even on the structure (XII) if B is the nucleus carrying the substituents Even the diazocoupling of 2,7-dihydroxynaphthalene at positions 1 and 8 (Ruggli and Courtin²³) is not incompatible with the structure (XII) if it be assumed that substitution first occurs at C_1 and then following a rearrangement to the alternative unsymmetrical structure at C_8 Hence Fieser and Lothrop²⁴ studied the behaviour of 1,8-dialkyl-2,7-dihydroxynaphthalene (XIV) and 1,5-dialkyl-2,6-dihydroxynaphthalene (XV) and found that they do not couple and that their allyl ethers do not rearrange This furnishes conclusive proof regarding the distribution of bonds in the entire molecule They are arranged as in Erlenmeyer's representation and do not change under the above conditions

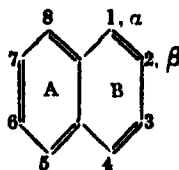
Thus far all the observations have gone to support the idea of the symmetrical structure (XI) The study of the dipole moments of some chlorinated naphthalenes by Hampson and Weissberger,²⁵ however, cast the first doubt on the above conclusion. According to them "each C-Cl bond in the chloronaphthalenes is directed as from the centre of the ring; if there is any fixation of single and double bonds in naphthalene it is not revealed in the direction of the substituents" Further evidence on the same lines was forthcoming from the work of Arnold and Sprung²⁶ who concluded from the values of the ionisation constants of isomeric *o*-hydroxy-naphthaldehydes that while a double bond was largely present between C_1 and C_2 ,

the presence of valence isomers with a double bond between C_2 and C_3 was also indicated. Also Baker and Carruthers²⁷ found a high degree of chelation not only in 2-acetyl-1-naphthol and 1-acetyl-2-naphthol (XVI) but also in 3-acetyl-2-naphthol (XVII). In the last compound the structure is definitely unsymmetrical with a double bond between C_2 and C_3 . In the case of these hydroxy-aldehydes and ketones the change is probably brought about as the result of chelation. Purely chemical evidence for the presence of a double bond between C_2 and C_3 are the conversion of sodium β -naphthoxide to the 3-carboxylic acid (Schmitt and Burkard²⁸) and the bromination of 1-bromo-*p*-toluenesulphon-2-naphthalide in the 3-position in pyridine solution (Bell²⁹). The formation of 3-iodo-1-nitronaphthalene indirectly from 1-nitro-2-naphthyl-amine (Hodgson and Elliot³⁰) is also another instance of the reactivity of the 3-position in a 2-substituted naphthalene.

From the comprehensive data presented above regarding the behaviour of naphthalene derivatives it is clear that though the double bonds exhibit very marked tendency to be located as in the symmetrical Erlenmeyer formula the alternative positions are not altogether excluded. The characteristic properties of fixation are noticed in this ring system far more prominently than with the simpler benzene derivatives.



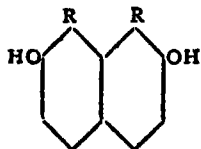
(XI)



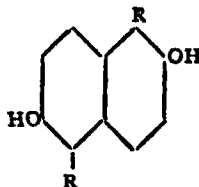
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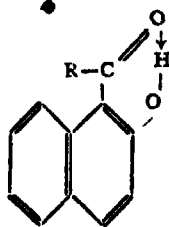
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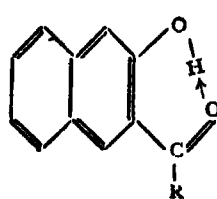
(XIV)



(XV)



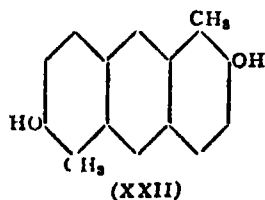
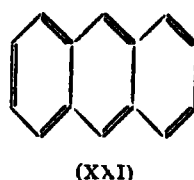
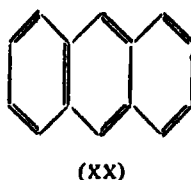
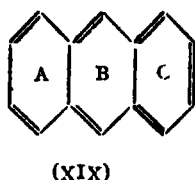
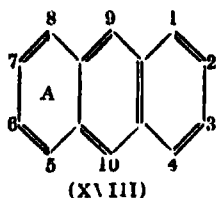
(XVI)



(XVII)

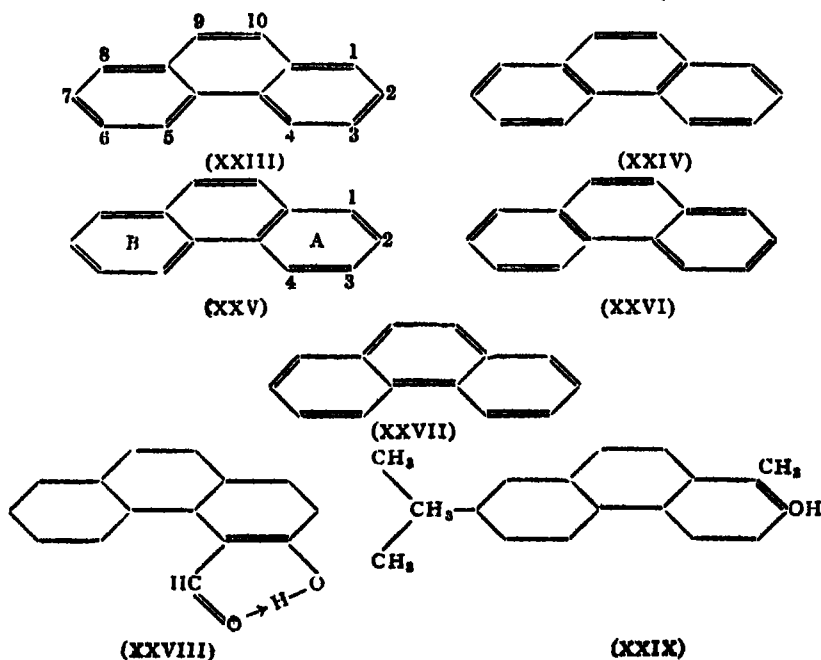
Anthracene — Not much critical work has been done on polynuclear condensed ring systems. It was Armstrong who first put forward the view that in anthracene there is present at least one ring (A) which contains only two double bonds and which together with the ethylenic linkages extending into the central nucleus constitutes an *o*-quinonoid or dihydrobenzenoid

system of linkages. All the four stable valence bond structures (XVIII, XIX, XX and XXI) for anthracene are expressive of this idea. But (XVIII) and its counterpart (XX) are more plausible since these structures are on the whole more aromatic than (XIX) and its counterpart (XXI). With a view to test this, Fries *et al*³¹ studied the bromination of 2,6-dihydroxy-anthracene and obtained the 1,5-dibromo derivative, but though this result supports formula (XVIII) it is not incompatible with (XIX) if we assume that after substitution in one ring (A) the bonds undergo a rearrangement so as to confer on ring (C) the same structure as is initially present in (A) and *vice versa*. Hence Fieser and Lothrop³² sought unequivocal evidence by studying the properties of 1,5-dimethyl-2,6-dihydroxy-anthracene (XXII). The failure of this compound to couple with diazotised amines definitely proved that in the anthracene structure the bonds are distributed as in (XVIII) and that the arrangement is immobile.



Phenanthrene — Five stable valence bond structures are possible for phenanthrene as in (XXIII–XXVII) of which (XXV) and (XXVI) are equivalent. Mere inspection reveals that all the three rings tend to approach the ideal aromatic condition only according to the second representation (XXIV). The logical consequence would be that this structure would make a greater contribution to the resonance energy of the hydrocarbon than the others and the reactions and other behaviour of phenanthrene would be more in accord with it than with any of the other structures. Critical evidence which can throw light on this problem is neither exhaustive nor even adequate. The great ease with which the 9,10-quinones are formed from phenanthrene and its derivatives indicates the presence of a double bond between these positions and thus definitely eliminates formula (XXVII). Smith³³ observed that 3-phenanthrol-4-aldehyde did not couple with diazotised amines simulating the behaviour of 1-methyl-2-naphthol; the evidence

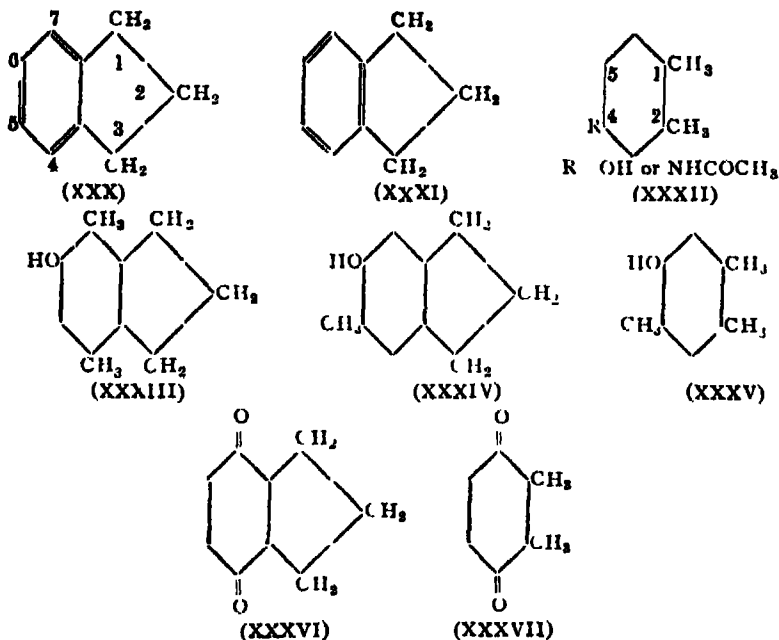
in this case is complicated by the existence of chelation as shown in (XXVIII). Recently Fieser, Young and Newman³⁴ have found that the allyl ethers of 2- and 3-phenanthrols undergo the Claisen transformation smoothly but the transformation products (obviously 1-allyl-2-phenanthrol and 4-allyl-3-phenanthrol) do not couple with diazotised amines and the allyl ether of the former does not again rearrange on heating. These evidences show that in phenanthrene the bonds are located as in (XXIV) or (XXV) [in the latter case if the substituents mentioned above are attached to ring (A) and not to ring (B)] and that structure (XXIII) is incompatible with these reactions. Though the behaviour of phenanthrene derivatives containing substituents in both the end nuclei does not seem to have been recorded, considerations of symmetry would dictate that (XXIV) is probably the nearest approach to the true configuration of phenanthrene rather than (XXV) or (XXVI). In fact belief in the rigid and unalterable distribution of the bonds of phenanthrene as in (XXIV) and in the infallibility of the diazo-coupling method for the location of double bonds has become so strong that this procedure has been employed by Fieser *et al*³⁴ to assign the constitution of 2-retinol (XXIX) to the compound previously known as A-retinol. This compound had been prepared by Komppa and Wahlfors³⁵ and the chief argument in support of the constitution assigned by Fieser *et al* was its inability to couple with diazotised amines.



Hydrindene.—The earlier evidence on hydrindene seemed to favour the idea that it has a rigidly fixed bond structure with a single bond common to the two rings but more recently this has not been found to hold good in all cases of hydrindene derivatives. From theoretical considerations Mills and Nixon³⁶ concluded that in hydrindene the form with a common single bond (XXX) should be the more favoured structure and in support of this they showed that in 5-hydroxyhydrindene and 5-acetamidohydrindene it is the 6th position that is reactive to the almost complete exclusion of the 4th. Similar results had been obtained even as early as 1926 by Borsche and Bodenstein.³⁷ They found that 5-acetamidohydrindene gave the 6-nitro and 6-bromo derivatives on nitration and bromination respectively. These evidences, however, lose much of their significance when the behaviour of 4-hydroxy-1,2-dimethylbenzene and 4-acetamido-1,2-dimethylbenzene (XXXII) is considered. These compounds are reactive only in position 5^{38,39} so that even in the 5-substituted hydrindene derivatives mentioned above the mere chemical effect of the methylene groups may be enough to explain adequately the formation of 6-substituted hydrindenes without any help from steric effects consequent on the fusion of the benzene ring with the 5-atom ring. Unambiguous evidence was therefore sought in the value of the dipole moment of 5,6-dibromohydrindene by Sidgwick and Springall.⁴⁰ They found for the Br-C-C-Br system of this compound a smaller value of the dipole moment than for the same system in *o*-dibromobenzene or in dibromo-*o*-xylene, thus proving definitely that there is no free resonance in hydrindene and that the rings have a common single bond. The same conclusion was arrived at by the application of the rigid chemical method developed by Fieser.⁴⁰ 6-Hydroxy-4,7-dimethylhydrindene (XXXIII) gave azo-dyes with diazotised amines but not 6-hydroxy-5-methylhydrindene (XXXIV). On the other hand pseudocuminol (XXXV) was able to couple with diazonium salts. Since chemically (XXXIV) and (XXXV) are similar the difference in the coupling capacity of the two compounds should be attributed to stereochemical effects. Obviously, owing to the fusion of the benzene ring with the polymethylene ring in (XXXIV), the C₈-C₇ link cannot behave like a double bond, in other words, the bonds of hydrindene are arranged as in (XXX) and this arrangement is unalterable. Further support to this conclusion was afforded by the results obtained by Arnold and Evans.⁴¹ By the ozonisation of hydrindene followed by catalytic hydrogenolysis of the ozonide they obtained glyoxal and succinic acid (obviously from cyclopentane-1,2-dione). This indicates that hydrindene exists mostly as (XXX). The alternative structure (XXXI) would have given glyoxal and α - α' -diketopimelic aldehyde or its oxidation products, none of which were detected in the final mixture.

Results not entirely supporting the rigid structure given above were first obtained by McLeish and Campbell¹⁸. Besides finding that the bromine atom in 6-bromo-5-nitrohydrindene was highly reactive as mentioned above they noticed that the 4-bromo isomer also exhibited a feeble reactivity indicating a common double bond between the two rings (type XXXI). This was subsequently confirmed by Sandin and Evans¹⁹ who, working mainly with 5-amino-hydrindenes with bromine atoms in the *o*-positions, found both the 6- and 4-bromine atoms reactive though to varying degrees. These authors however added that any inference that might be drawn was in favour of (XXX) being the favoured structure. A similar conclusion was drawn by Arnold and Zaugg⁴² who found a higher oxidation-reduction potential for 4,7-hydrindenequinone (XXXVI) than for *o*-xyloquinone (XXXVII). This was attributed by these authors to a "positive Mills-Nixon type of partial double bond stabilisation" though the reasons for the use of the term 'partial' are not clear. More definite evidence pointing to structure (XXXI) for hydrindene was furnished by the experiments of Fieser and Lothrop⁴³ who found that 5-hydroxy-6-methylhydrindene could form azo-dyes under certain carefully controlled conditions. A quantitative study of the diazo-coupling reaction led the latter author⁴⁴ to the conclusion that hydrindene derivatives were inferior to β -naphthol in coupling capacity and more comparable to 2:4-dimethylphenol. The smooth Claisen rearrangement of 5-allyloxyhydrindene when the 4- and 6-positions were separately blocked by methyl groups also lent support to the conclusion that the bond fixation in hydrindene derivatives is not very rigid⁴⁴. The formation of 4,6-dibromo-5-amino-hydrindene by direct bromination of 5-aminohydrindene (Borsche and Bodenstein³⁷) and the comparative values of the dissociation constants of 5-hydroxy-6-nitrohydrindene and of 2-nitrophenols (Arnold and Evans⁴⁵) also show non-stabilization of double bonds as a result of ring fusion. Again from a study of the depression in melting point on wetting Baker⁴⁶ found that both 5-acetyl-6-hydroxy- and 5-acetyl-4-hydroxy-hydrindenes are chelated though to varying degrees. These compounds can exhibit chelation only if a single and a double bond respectively can be brought into being in common between the two rings in accordance with structures (XXX) and (XXXI) thereby enabling the chelate ring to possess a double bond. It may therefore be concluded that in hydrindene the structure with a common single bond is the more favoured though the other alternative is not excluded.

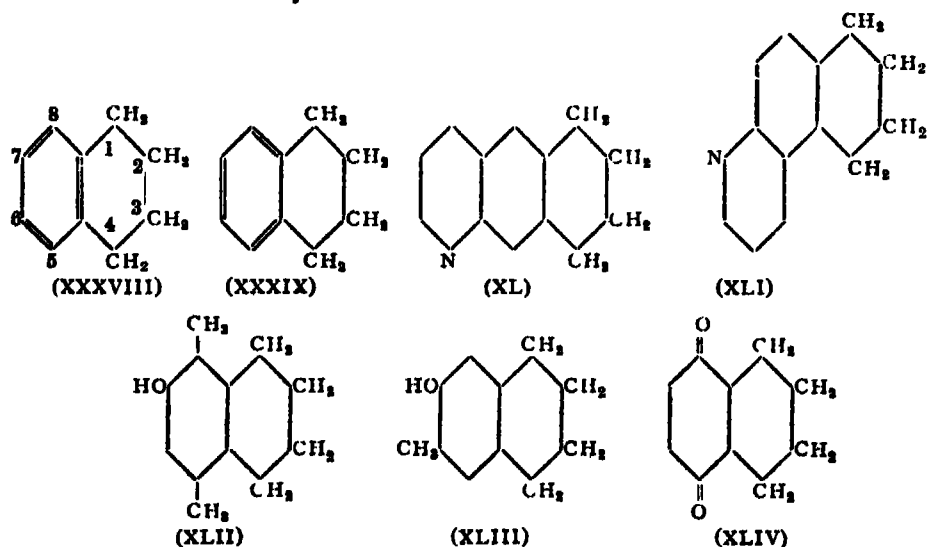
Tetralin—According to the theoretical considerations developed by Mills and Nixon³⁸ tetralin should have a predominant structure in which a double bond is common to the two rings (XXXVIII). In support of their



conclusion these authors quoted the previous findings of Schroeter⁴⁷ and of Smith⁴⁸ that 6-hydroxy- and 6-acetamidotetralin gave 5-substituted compounds in bromination and diazo-coupling experiments. Another evidence favouring this idea is the presence of a positive bromine atom in 5-bromo-6-aminotetralin (Sandin and Evans¹⁹) and in 5-bromo-6-hydroxy-7-aminotetralin (Schroeter⁴⁷). This method however does not seem to be altogether satisfactory and consistent, since McLeish and Campbell¹⁸ found proof for the alternative conclusion (common single bond, type XXXIX) in the behaviour of 6-bromo-5-nitrotetralin (unreactive) and 6-bromo-7-nitrotetralin (reactive). A result which is in conformity with the latter observation is the formation of 6-hydroxy-7-nitrotetralin from 6-hydroxy-tetralin (Thomas and Kross⁴⁹). Thus tetralin seems to be capable of reacting in the alternative structural form (XXXIX) with equal facility.

That tetralin is really to be considered as made up of a mixture represented by the two structures was evident from the work of V. Braun and Grüber⁵⁰ who subjected 6-amino-tetralin to the Skraup reaction and obtained a mixture of the linear and angular varieties of the tricyclic compound (XL and XLI). The more subtle methods of investigation are also largely in favour of the idea that in tetralin there is no fixation of the double bonds and that there is resonance in the purely aromatic sense. Thus, Sidgwick and Springall⁵¹ found that the Br-C-C-Br system in 6:7-dibromotetralin

had a value for the dipole moment equal to that in *o*-dibromobenzene and dibromo-*o*-xylene Fieser and Lothrop⁴⁰ found that both 7-hydroxy-5, 8-dimethyltetralin (XLII) and 7-hydroxy-6-methyltetralin (XLIII) could couple with diazotised amines, while in quantitative experiments using the method of diazo-coupling tetralin derivatives were less reactive than β -naphthol and more akin to 2,4-dimethyl-phenol (Lothrop⁴⁴) Further Arnold and co-workers found 6-hydroxy-7-nitrotetralin and *o*-nitrophenols to have the same value for the dissociation constant⁴⁵ and 1, - 2, - 3, - 4- tetrahydronaphtho-5, 8-quinone (XLIV) and *o*-xyloquinone (XXXVII) to have nearly equal oxidation-reduction potentials⁴² showing non-stabilisation of the double bonds in the tetralin system

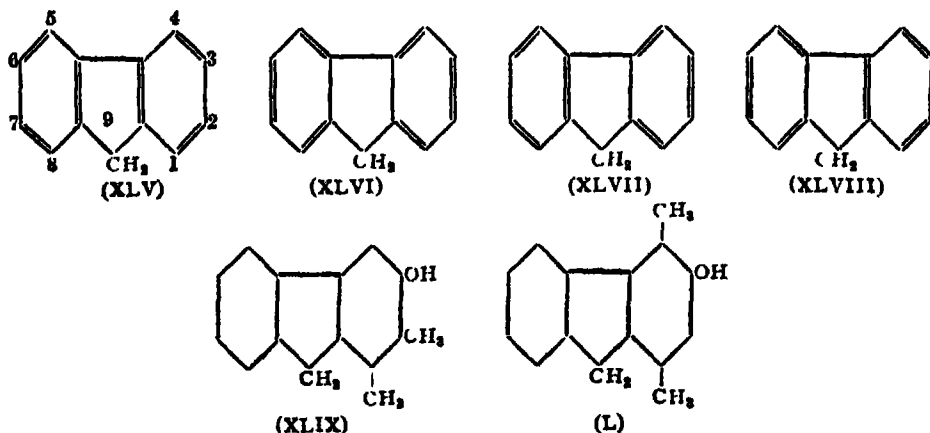


Fluorene—There are four important structures that can be formulated for fluorene. Of these the symmetrical ones (XLV) and (XLVI) would be the more plausible though the unsymmetrical ones (LXVII) and (LXVIII) cannot be altogether ignored in the absence of positive evidence in favour of such elimination. (XLV) represents the fluorene molecule as essentially derived from cyclopentadiene while (XLVI) looks more like a cyclopentane compound. Both of them contain an unbroken chain of conjugated double bonds and would have considerable stability.

On the basis of refractivity studies Auwers *et al*^{51,52} concluded that the aromatic rings in fluorene must be classed as similar to naphthalene and anthracene at least qualitatively. From nitration experiments Ananthakrishnan and Hughes⁵³ obtained evidence for considering fluorene as dibenzocyclopentadiene. Subsequently Hughes, LeFevre and LeFevre⁵⁴ concluded

from studies of dipole moments that their data did not point to any specific configuration for fluorene whose structures may be flat degenerate forms between (XLV) and (XLVI)

On the chemical side the evidence which is incomplete, inasmuch as it refers to only one of the benzene rings and not simultaneously to both, does not point to any rigid structure represented by either (XLV) or (XLVI). Thus γ -2-fluorene-butyric acid and α -2-fluorenebenzoic acid close up rings in such a way that the 3-position is involved^{55,56}. These point to structure (XLVI) for fluorene. On the other hand 2-acetoxyfluorene and 2-acetoxyfluorenone undergo the Fries migration to give 1-acetyl-2-hydroxy compounds⁵⁷ thus pointing to structure (XLV). However, a great many fluorene derivatives behave as though there is no fixation of the double bonds in any position. Thus, Lothrop⁵⁸ found that 2-allyloxyfluorene underwent the Claisen transformation to give a mixture of isomers supposed to be the 1- and 3-allyl-2-hydroxyfluorenes, both 1 2-dimethyl-3-hydroxyfluorene (XLIX) and 1 4-dimethyl-3-hydroxyfluorene (L) coupled with diazotised amines and their allyl ethers smoothly underwent the Claisen transformation thus showing that either of the α -positions of 3-hydroxyfluorene can behave as a reactive centre in these reactions. Again 2-allyloxyfluorenone behaved just like 2-allyloxyfluorene in the Claisen transformation giving a mixture of isomeric products,⁵⁷ and the Kolbe's reaction with 2-hydroxyfluorene gave two isomeric acids (obviously the 1- and 3-carboxylic compounds)⁵⁹. Thus the balance of evidence seems to be in favour of the idea that in fluorene there is little fixation of the nuclear bonds just as in diphenyl

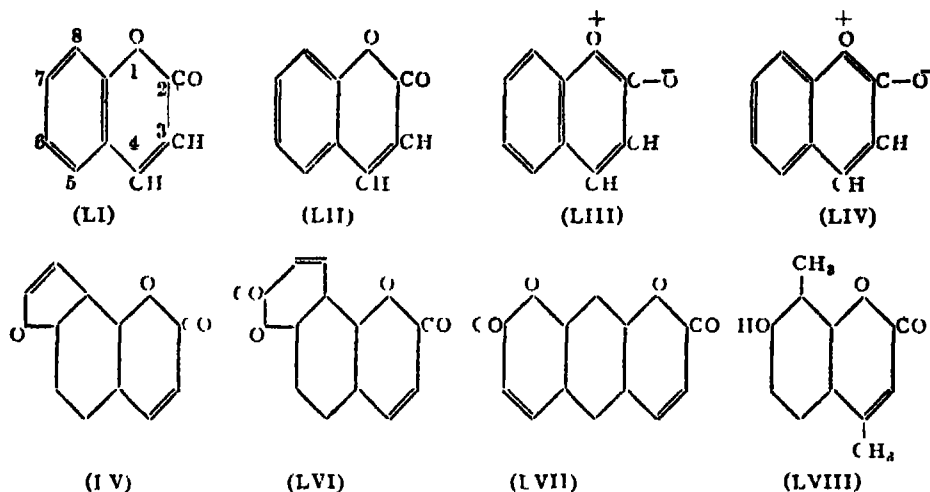


Coumarin and Chromone—Though in coumarin itself substitution invariably takes place in the 6th position, in 7-hydroxycoumarins it is exclusively in the 8th position. When attempts are made to build up fresh rings

starting from 7-hydroxy-coumarins, it is the 8th position that is involved in the ring-formation. Thus employing 7-hydroxycoumarin and bromo-acetal Späth⁶⁰ obtained angelicin (LV). Rangaswami and Seshadri⁶¹ similarly found that the Pechmann condensation between 7-hydroxycoumarins and malic acid or acetoacetic ester gave mostly the angular coumarino- α -pyrones (type LVI). Again attempts to introduce an aldehyde group into 7-hydroxycoumarins gave the 8-aldehydes^{61,62}. All these show that 7-hydroxycoumarins react in the form (LI). The most reliable evidence for this structure, however, comes from the work of Baker and Lothian³ who found that 7-allyloxy-4-methylcoumarin undergoes the Claisen transformation to give 7-hydroxy-8-allyl-4-methylcoumarin thus proving conclusively that there exists a double bond between the 7- and 8-positions.

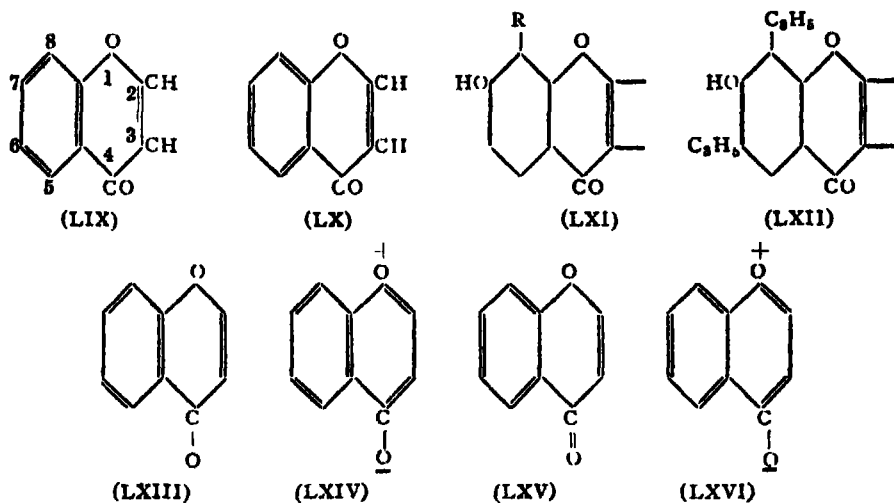
Evidence which does not fall into line with the above was first obtained by Limaye⁶³. He found that when 4-methyl-7-acetoxycoumarin was subjected to Fries migration, the 8-acetyl-7-hydroxy compound which was the major product was accompanied by a small quantity of the 6-acetyl-isomer. The simultaneous formation of the angular coumarino- α -pyrone (LVI major product) and the linear isomer (LVII, minor product) from the Pechmann condensation using umbelliferone and malic acid (Rangaswami and Seshadri⁶¹) corroborates the above observation and shows the slight but significant reactivity of the 6th position in umbelliferone. The last-mentioned authors have applied Fieser's technique to the coumarin ring system and obtained unequivocal evidence on the distribution of the single and double bonds⁶⁴. They have found that 7-hydroxy-4,8-dimethylcoumarin (LVIII) couples with diazotised *p*-nitraniline and forms with mercuric acetate a mercury derivative which contains 2-acetoxy-mercuri groups replaceable by bromine atoms. The allyl ether and acetyl derivative also smoothly undergo the Claisen transformation and Fries migration respectively. All these reactions can be explained only on the assumption of a reactive 6-position which is possible only if the bonds can take up positions as depicted in (LII). Thus in coumarins while the normal structure corresponds to (LI) the other is not precluded.

From a study of dipole moments Rau⁶⁵ concluded that coumarin exists in the excited state mainly as (LIII). Besides many others the alternative structure (LIV) (not mentioned by this author) is also possible in which the situation in the lactonic part is the same. A comparison of the two forms clearly shows that on the whole (LIII) represents a more aromatic structure than (LIV) and will tend to be the more important of the two forms in entire agreement with results deduced from chemical reactivity.



The theoretical considerations of the structure of chromones and flavones (benzo- γ -pyrones) and the experimental study follow on lines closely similar to those applied to the coumarins (benzo- α pyrones). The great reactivity of the 8th position in 7-hydroxy-chromones is evident from the formation of the 8-aldehyde from 7-hydroxy-3-methoxyflavone by the action of formylating agents (Rangaswami and Seshadri⁶⁶). Again it is the 8th position that is involved in the Fries migration of 7-acetoxy-2-methylchromone (Wittig, *et al*⁶⁷) or its 3-acetyl derivative (Baker⁶⁸) and in the Claisen transformation of the allyl ethers of 7-hydroxyflavone and 7-hydroxy-2-methyl-3-methoxychromone (Rangaswami and Seshadri⁶⁹). These suggest a fixation of the double bonds as in (LIX). But the 8-allyl-7-hydroxy-compounds (LXI, R = allyl) obtained from the above Claisen transformations give allyl ethers which are capable of undergoing further Claisen rearrangement to give rise to the 6,8-diallyl-7-hydroxy-chromones and flavones (LXII)⁶⁹. This indicates that the nuclear bonds are capable of redistribution as in type (LX). Further support for this conclusion is afforded by the capacity of 8-methyl-7-hydroxyflavone and its 3-methoxy derivative (LXI, R = methyl) and of 8-allyl-7-hydroxyflavone and 8-allyl-7-hydroxy-2-methyl-3-methoxy chromone (LXI, R = allyl) to couple with diazotised *p*-nitraniline⁶⁹. Thus the initial distribution and realignment of bonds in chromones are quite analogous to the case of coumarins.

A close examination of the formulæ (LXIII) to (LXVI) leads us to the same conclusion. (LXIV) represents the reactive or excited state of the molecule and it exhibits the maximum aromatic characteristics. (LXIII) corresponds to a *p*-quinone structure. In both these there exists a double



bond in common between the two rings and as a consequence the disposition of the other bonds in the benzene part is fixed. Structures (LXV) and (LXVI) represent other possibilities and have a single bond in common between the rings; but these are obviously less stable structures devoid of the maximum conjugation and their contribution to the behaviour of the molecule will be small. Though small it seems to be appreciable and definite as indicated by the experimental results recorded above.

The simultaneous reactivity of the 6- and 8-positions in the coumarins and chromones indicating the occurrence of the two alternative positions of the double bonds has been to some extent indicated by recent experiments. The formation of 6,8-disubstituted derivatives from 7-hydroxy-coumarin during mercuriation, bromination and nitration using excess of the reagents does not really have much significance in this connection, it is possible to explain these reactions by assuming that first the attack is initiated at position 8 of the form (LI), the product subsequently changes into the form (LII) and then reacts with more of the reagent in position 6 to give the 6,8-disubstituted compounds, provided of course that the physical conditions are not adverse to the progress of this second stage of the reaction (*vide* Rao, Sastri and Seshadri⁷⁰). On the other hand the simultaneous formation of the 8- and 6-acetyl-7-hydroxy compounds by the Fries migration of 7-acetoxy-4-methylcoumarin (Limaye⁶⁹), and of the angular and linear coumarino- α -pyrones by the Pechmann condensation of 7-hydroxycoumarin and malic acid (LVI and LVII⁶¹), show that the 8- and 6-positions can be simultaneously reactive in these compounds. In support of this there is the evidence of Rangaswami and Seshadri⁷¹ who have carried out quantitative diazo-

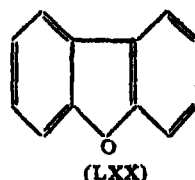
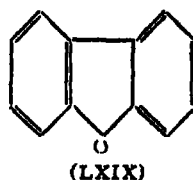
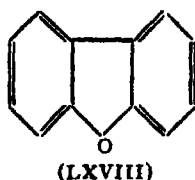
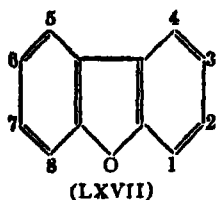
coupling experiments to study this question. Starting with 7-hydroxy-4-methylcoumarin and 7-hydroxy-2-methyl-3-methoxychromone and employing just one molecular proportion of diazomium salts they have obtained dyes whose compositions show that bis-azo-dye formation has taken place. This is not possible if the 6th position can become reactive only after the 8th has completely reacted, since in such a case the quantity of reagent used would have been completely used up by the 8th position. The fact that bis-azo-dyes were not formed in the case of all the coumarins and chromones studied under the influence of only one molecular proportion of the reagent does not invalidate the above conclusion regarding the simultaneous reactivity of the 6- and 8-positions. Obviously the substituent groups in these compounds are not altogether without an effect on the mobility of the nuclear bonds. This statement receives support from similar observations by the same authors in other types of reactions as well. Thus though umbelliferone and malic acid gave a mixture of coumarino-pyrones under the conditions of the Pechmann condensation only the angular compounds (reactive 8-position) were formed from 4-methyl-umbelliferone and malic acid or ethyl acetoacetate.⁶¹

Dibenzofuran

Four structures (LXVII to LXX) are important for dibenzofuran. LXIX and LXX which are equivalent among themselves are not likely to be as important as the other two inasmuch as they assume that the molecule is unsymmetrical. As between LXVII and LXVIII the former represents the hydrocarbon as a furan derivative, the latter as a dihydrofuran derivative. For maximum stability each component ring should have the maximum aromatic configuration and hence (LXVII) would represent the most important canonical structure. At the same time we find a high degree of conjugation even in (LXVIII) and hence the contribution of this form to the resonance energy would certainly come next in importance to that of (LXVII). Thus we seem to be having here a case similar to fluorene, the bonds can take up either of the alternative positions with equal ease.

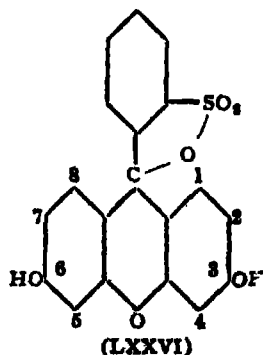
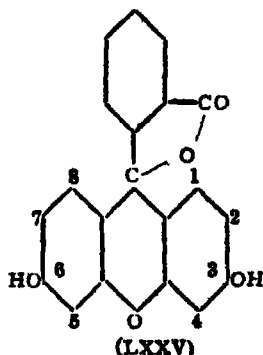
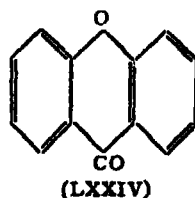
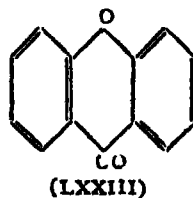
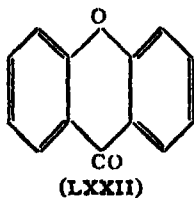
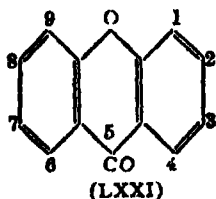
A complete chemical investigation of this question would involve the study of substitution not only in one part of the molecule but simultaneously in both the end rings. Such definite proof, however, seems to be lacking. The available evidence, mostly the work of Gilman and his school, shows that there is no specially favoured disposition for the bonds, though it refers only to one of the benzene rings. The bromination and nitration of hydroxy-, methoxy- and acetamido-dibenzofurans⁷² and the diazo-coupling of 2-hydroxy-, 3-hydroxy- and 4-hydroxy-dibenzofurans⁷³ give results some

of which are in accord with formula (LXVII) while the rest are expressive of formula (LXVIII)



Xanthone and Xanthene

Four important structures (LXXI to LXXIV) are possible for xanthone of which, by analogy with chromones, the first would be expected to be the nearest approach to the true structure of the molecule. LeFevre⁷⁴ found that the dipole moments of 2,7-dibromo- and dinitroxanthones are in good agreement with the structure (LXXI) and further that the bonds are almost completely fixed as depicted in that formula. If fluorescein (LXXV) can be considered as a xanthene derivative then valuable information can be gathered regarding the distribution of bonds in this system from the reactivity of the dye as pointed out by Sandin, *et al*⁷⁵. The data available regarding this compound have one welcome feature, derivatives containing substituents in both the benzene rings are easily available and are amenable to experimental study so that it is possible to get a complete picture of the entire molecule. Sandin and co-workers thus found that bromination of fluorescein and sulphone-fluorescein (LXXVI) produced 4,5-disubstituted

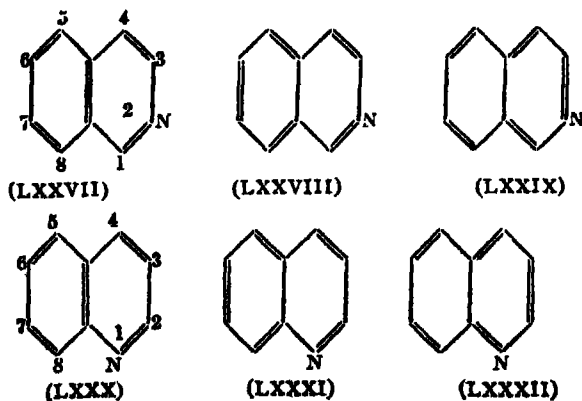


compounds (Orndorff, *et al*⁷⁶; Sandin *et al*⁷⁵) Further in tetrabromofluorescein and 4 5-dibromo-2 7-dichlorofluorescein, the 4 and 5 bromine atoms alone were found to be reactive (Sandin, *et al*⁷⁵) The dinitration of fluorescein again yielded the 4 5-dinitro compounds (Hewitt, *et al*⁷⁷) and the formation of bis-azo-dyes from fluorescein involved the same two positions (Igraffia⁷⁸) All these suggest structures rigidly fixed as shown in (LXXI) for the xanthone system

Quinoline and Isoquinoline

Chemical work relating to these systems was done as early as 1922 Three structures are possible for iso-quinoline (LXXVII to LXXIX) The work of Mills and Smith⁷⁹ showed that the methyl group in 1-methyl-iso-quinoline was reactive but not the methyl in 3-methyl-iso-quinoline Similarly a chlorine atom in the 1-position was easily replaced by hydrogen on treatment with red phosphorus and hydriodic acid but not when it was present in the 3-position These prove the existence of a double bond between positions 1 and 2 in isoquinoline and of another double bond between 3 and 4 Regarding the nature of the common link and of the bonds in the benzene part in iso-quinoline positive evidence is lacking, but it may probably be safe to assume that (LXXVII) is the closest approximation to the true structure of the molecule

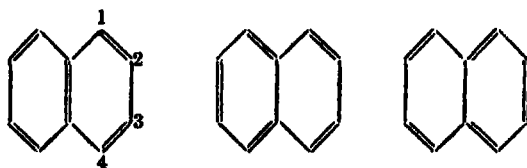
Mills and Smith⁷⁹ were of the opinion that in quinoline also the distribution of bonds should be just as in iso-quinoline, capable of representation by formula (LXXX) The theoretical structures are also of the same type as in iso-quinoline and their relative importance would be of approximately the same order of magnitude Definite evidence was obtained by LeFevre and LeFevre⁸⁰ who concluded from the study of dipole moments of quinoline derivatives that the mobilities of the single and double bonds in quinoline derivatives are so diminished by ring fusion that the skeleton is best



formulated as (LXXX) and this statement seems to hold good except when dynamic isomerism is rendered possible as in the case of 2-methylquinoline

Discussion of Results and Conclusion

From the results presented in the foregoing pages it is clear that there has been a large amount of data of a chemical as well as physical nature relating to the question of the fixation of aromatic double bonds. It is possible that some of them might undergo modifications as a result of careful revision. This is due to the inherent difficulties of experimental technique in this line of work. Taking into consideration all factors there appears to be sufficient justification for concluding in favour of fixation of the double bonds. This fixation seems to be of varying degrees, being (1) very weak when chelate rings are the cause of fixation, (2) more prominent when heterocyclic rings are involved and (3) more or less rigid in polynuclear aromatic structures such as naphthalene, anthracene, etc. Apparently these statements may be objectionable from the physicist's point of view since it may be considered not to be in consonance with the discoveries that benzene and naphthalene are absolutely plane symmetrical structures. But the theory of resonance which has been developed and employed successfully during recent years seems to eliminate all difficulties. These ideas have been very adequately summed up by Pauling in his well-known recent book "*The Nature of the Chemical Bond*" (1st edition, pages 131-35). It has been shown that the stability and characteristic aromatic properties of benzene can be attributed to resonance of the molecule between two Kekule structures, each of the six bonds in the ring acquiring half a double bond character. For naphthalene three stable valence bond structures can be formulated as below



As a consequence there is brought about considerable difference between the characteristics of the different bonds. Thus the bond between 1- and 2-positions has $\frac{2}{3}$ double bond character whereas the one between 2- and 3-positions has only $\frac{1}{3}$ double bond character with the result the former behaves very much like a double bond whereas the latter has very little double bond characteristics. This results in an enormous difference in reactivity giving rise to the well-known phenomenon which has been described as 'fixation'. In the case of anthracene and phenanthrene the differences

between the bonds are even greater owing to the existence of larger numbers of valence bond structures. No correct prediction has obviously been attempted of the nature of the bonds when substituents which can produce powerful electromeric effects such as the hydroxyl, amino, bromo and nitro are introduced in these aromatic structures. It may however be expected that the differences between the bonds will be further accentuated. Similar explanations can be given of the effect of heterocyclic rings and of chelate rings. But this fixation can never be absolutely rigid since the other bonds also have very small but still appreciable double bond characteristics. And when the more reactive positions are protected, the feebler reactivity of the others is exhibited especially with powerful reagents and under favourable conditions.

The above remarks hold good even in the case of what is known as the "Mills-Nixon effect" where saturated carbon rings, attached to two ortho positions of a benzene ring, make it react as though the double bonds were fixed in one or the other of the alternative positions.

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THE KINETICS OF THE MUTAROTATION OF AMINOMETHYLENE-*d*-CAMPHOR

BY BAWA KARTAR SINGH

(The Chemical Department, The University of Allahabad, Allahabad)

AND

SAILESH CHANDRA SEN

(The Chemical Department, Ravenshaw College, Cuttack)

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THE mutarotation of aminomethylene-*d*-camphor in glacial acetic acid and in aqueous acetic acid solutions has been studied in this paper

Aminomethylene-*d*-camphor was first prepared by Bishop Claisen and Sinclair¹ Later Singh and Bhaduri² studied its rotatory dispersion in several solvents Iminomethylene-*d*-camphor was also prepared by Bishop Claisen and Sinclair (*loc cit*), but the yield was very poor Singh and Bhaduri (*loc cit*) obtained this substance in better yield by the condensation of aminomethylene-*d*-camphor with oxymethylene-*d*-camphor We have now discovered that it can be prepared very simply by dissolving aminomethylene-*d*-camphor in glacial acetic acid the conversion takes place in a short time and the yield is quantitative The change is complete in the cold (35°) within 1 hour and 40 minutes (Table I) The reaction is much hastened on boiling and the conversion is complete within 5 minutes It has been further observed that if aminomethylene-*d*-camphor is heated above its melting point, ammonia is given off and iminomethylene-*d*-camphor is formed

As the conversion of aminomethylene-*d*-camphor into iminomethylene-*d*-camphor takes place with measurable velocity in glacial acetic acid solution in the cold, and is accompanied by a change in its rotatory power, it has been found possible to determine the velocity constant of the reaction (Table I) The chemical reaction is found to be monomolecular and the mean value of *k*, the velocity constant, varies from 5.94×10^{-3} to 6.11×10^{-3} at four different concentrations ranging from about 0.4% to 1.6%

The mutarotation of aminomethylene-*d*-camphor in acetic acid of 90%, 80% and 75% concentration has also been determined Whereas mutarotation in glacial acetic acid solution is accompanied by a rise in rotatory power, there is first a rise followed by a fall in rotatory power in aqueous acetic acid solution (Tables II and IV). The small rise in rotatory power in aqueous

¹ *Ann.*, 1894, 281, 395

² *J. Ind. Chem. Soc.*, 1932, 9, 109.

acetic acid solution occurs in the first six or seven minutes of making up the solution (Tables II and IV), and after this brief period there is a gradual fall in rotation which becomes constant, but the value is different in the case of solutions of varying strength of acetic acid. If the polarimetric observation is delayed for about 7 minutes after making up the solution, the initial rise in rotatory power is not observed (Table III). The reaction in aqueous acetic acid solution does not follow the monomolecular equation. It is, therefore, clear that the reaction takes a somewhat different course in aqueous acetic acid solution. The reason for this anomalous behaviour is not, at present, quite clear, and further work for its elucidation is required. Whether the presence of water in acetic acid brings about racemisation, and may thus explain the erratic changes in rotatory power is still a moot point. Iminomethylene-*d*-camphor prepared from aminomethylene-*d*-camphor in glacial acetic acid solution and in dilute acetic acid (90% and 80%) has the same rotatory power in ethyl alcohol (Table V), but the yield in each case is different. It is maximum in glacial acetic acid and diminishes with its dilution with water.

Experimental

Aminomethylene-*d*-camphor (1 gr) is heated with 25 c.c. of glacial acetic acid for about 10 minutes. Water is then added to the solution when iminomethylene-*d*-camphor is thrown down. It is crystallised from ethyl alcohol as needles, m.p. 216°–218°. The yield being over 0.9 gr is almost quantitative. The *laevo* and racemic varieties of iminomethylene-camphor are obtained in the same way from *l*- and *dl*-forms of aminomethylene-camphor, m.p. 216–218° as in the case of the *d*-isomeride.

The solution for polarimetric observations was made by dissolving the given weight of aminomethylene-*d*-camphor in the solvent which had been previously kept in the thermostat at 35° C. The thermostat was heated electrically and its temperature was controlled by means of a toluene regulator. The temperature was read with a Beckmann thermometer, and was correct within 1/50th of a degree centigrade. The rotatory power was determined in a 2-dm. jacketed tube, through which water was circulated by means of an electrically-driven pump from the thermostat. The polarimeter was of the Adam Hilger triple field type, which carried a D V spectro-scope in the eye-piece. A vertical slit was used as a source of light at the polariser end, which was illuminated with a mercury arc.

The value of *k*, the velocity constant, is calculated from the monomolecular equation,

$$k = \frac{2.303}{t_y - t_x} \log \frac{[\alpha]_x - [\alpha]_\infty}{[\alpha]_y - [\alpha]_\infty},$$

the time being expressed in minutes.

TABLE I
Solvent Glacial Acetic Acid

I Series Concentration, g/100 c c = 0.3904

Time	$[\alpha]_{H_g 5461}^{25^\circ}$	$K \times 10^{-3}$	Time	$[\alpha]_{H_g 5461}^{25^\circ}$	$K \times 10^{-3}$
Initial	Not observed		15' 30"	611.2°	6.10
6' 5"	503.3°		16' 35"	620.4	6.10
7'	516.6	5.90	17' 35"	628.4	6.10
8'	530.4	5.94	19'	638.8	6.02
9'	543.3	5.92	21'	652.2	6.10
10'	555.8	6.03	24' 10"	669.8	5.89
11' 15"	569.9	5.86	25' 10"	674.9	6.14
12' 15"	580.4	5.83	29'	691.4	5.97
13' 15"	590.4	5.87	1 hr 40'	755.6	
14' 30"	602.1	5.88	∞ (160 hrs)	755.6	
			Mean		5.98

II Series Concentration, g/100 c c = 0.8296

Time	$[\alpha]_{H_g 5461}^{25^\circ}$	$K \times 10^{-3}$	Time	$[\alpha]_{H_g 5461}^{25^\circ}$	$K \times 10^{-3}$
Initial	Not observed		18'	609.3°	5.94
4' 40"	427.9°		19' 20"	620.8	6.11
6'	453.2	6.01	23' 20"	649.7	5.99
9'	503.9	6.03	24' 20"	655.7	5.83
10'	518.3	5.87	25' 40"	663.4	5.95
13'	557.8	6.05	26' 45"	669.2	5.95
14' 30"	575.1	6.08	29'	680.4	5.90
16'	590.6	5.96	∞	756.4	
17'	600.3	6.11	Mean		5.98

III Series Concentration g/100 c c = 1.2144

Time	$[\alpha]_{H_g 5461}^{25^\circ}$	$K \times 10^{-3}$	Time	$[\alpha]_{H_g 5461}^{25^\circ}$	$K \times 10^{-3}$
Initial	Not observed		15'	598.6°	6.06
4'	450.3°		16' 45"	613.5	5.62
5'	467.6	5.78	17' 45"	621.7	5.87
6'	484.5	5.99	19'	631.6	6.04
7' 20"	505.8	6.10	20'	639.0	6.04
8' 25"	522.2	6.23	21'	645.8	5.97
9' 40"	539.4	6.06	24'	664.5	6.10
10' 40"	551.9	5.81	25'	669.8	5.85
11' 40"	563.6	5.87	30'	691.7	5.74
12' 40"	574.8	5.94	∞	757.6	
13' 40"	585.2	5.87	Mean		5.94

IV Series Concentration, g/100 cc = 1.6488

Time	$[\alpha]_{\text{H}_2\text{O}}^{25^\circ}$	$K \times 10^{-2}$	Time	$[\alpha]_{\text{H}_2\text{O}}^{25^\circ}$	$K \times 10^{-2}$
Initial	Not observed				
2' 40"	433.6°		15' 15"	606.5°	5.94
4'	458.9	6.08	17' 35"	629.0	6.05
5'	476.1	5.94	18' 55"	636.5	5.85
6' 20"	498.2	6.11	20'	645.3	6.95
8' 40"	532.2	6.01	22'	658.1	6.01
10' 40"	558.0	6.07	23'	664.1	6.20
13'	584.8	6.17	∞	758.1	
				Mean	6.11

TABLE II

Solvent 90% Acetic Acid

Concentration, g/100 cc = 0.3672

Time	$[\alpha]_{\text{H}_2\text{O}}^{25^\circ}$	Time	$[\alpha]_{\text{H}_2\text{O}}^{25^\circ}$
Initial	Not observed		
3' 10"	612.7°	20 hrs.	571.9°
4'	631.8	44 "	544.7
7' 15"	640.0	67 "	537.9
8' 10"	633.2	92 "	510.6
9'	626.4	164 "	463.0
16'	623.6	188 "	456.1
32' 20"	612.7	212 "	456.1
		236 "	456.1

TABLE III

Solvent 80% Acetic Acid

Concentration, g/100 cc = 0.3788

Time	$[\alpha]_{\text{H}_2\text{O}}^{25^\circ}$	Time	$[\alpha]_{\text{H}_2\text{O}}^{25^\circ}$
Initial	Not observed		
5' 50"	572.9°	18 hrs	402.6°
6' 50"	567.6	28 "	376.2
10'	559.7	42 "	366.9
17' 5"	554.4	93 "	348.5
1 hr 44'	534.6	139 "	344.5
3 hrs 8'	514.8	221 "	333.9
5 " 33'	493.7	317 "	332.6
		365 "	332.6

TABLE IV

Solvent 75% Acetic Acid

Concentration, g/100 c c = 0.3788

TABLE V

Solvent Ethyl Alcohol

Concentration, g/100 c c = 0.4360

Time	$[\alpha]_{D}^{25}$	Iminomethylene- <i>d</i> -camphor prepared from	$[\alpha]_{D}^{25}$
Initial	Not observed	Glacial Acetic Acid Solution	636.6°
3' 30"	510.8°	90%	634.1
4' 30"	521.5	80% " "	632.4
6' 30"	516.1		
12' 30"	514.8		
17' 30"	513.5		
1 hr 23'	493.8		
3 hrs 30'	468.6		
22 " 47'	349.8		
131 "	297.0		
151 "	297.0		

The initial time of reading, given in the Tables, from the commencement of the solution, was not the same, but varied in different experiments.

Further work on this compound and its *laevo*-isomeride is in progress at Allahabad.

KINETICS OF SOL-GEL TRANSFORMATION

Part V. The Influence of Different Coagulating Electrolytes on the Setting of Ferric Phosphate Gel

BY HIRA LAL DUBE, M SC , D PHIL

(*Chemical Laboratory, Meerut College, Meerut*)

AND

SATYA PRAKASH, D SC , F A Sc

(*Chemical Laboratory, University of Allahabad*)

Received July 5, 1941

In previous publications of this series,¹ the authors have studied the expression $\log S = \log R + p \log C$, where S is the inverse setting time of the jelly when coagulation has been affected with an electrolyte of concentration C R and p are constants, the significance of which has been mentioned in previous papers. We have shown that the expression is valid for almost all the jellies obtained by slow gelation of sols in presence of varying concentrations of electrolytes. The influence of dilution, temperature and purity of sols on the setting of these jellies has been investigated already. In the present communication, we have studied the influence of various coagulating ions on the setting of ferric phosphate jellies.

The quantitative expression for the coagulating power of electrolytes, especially with reference to the valency of coagulating ions, was given by Whetham.² According to him, if discharge requires the presence of ions of opposite charge in the vicinity of the particle, there must be present simultaneously 2 trivalent, 3 divalent or 6 monovalent ions. Since the probabilities for simultaneous presence are proportional to the corresponding powers of the concentrations, Whetham arrived at the following formula for the flocculating concentrations of monovalent, divalent and trivalent ions, c_1 , c_2 and c_3 .

$$1/c_1 + 1/c_2 + 1/c_3 = 1/x + x^2$$

Chakravarti, Ghosh and Dhar³ have modified the Whetham's equation slightly. According to them, if N_1 , N_2 , N_3 , ... N_x be the precipitating concentrations of uni-, bi-, tri-, ... x -valent ions, then

$$N_1 + N_2 + N_3 + \dots + N_x = 1 + \frac{1}{2} \alpha + \frac{1}{3} \alpha^2 + \dots + \frac{1}{x} \alpha^{x-1},$$

where $\alpha = e^{\frac{-qe/Dr}{kT}}$

These expressions are only valid when the coagulation process does not involve any complication and is guided by the mere electric attraction between the colloidal particle and the ion. The possible complications in the case of an ordinary coagulation are the adsorption of similarly charged ion, the marked adsorbability of the precipitating ion and the large differences in the ionic velocity of the coagulating ions. When applied to the coagulation processes leading to the formation of a jelly, all these expressions are bound to fail. The process of jelly formation starts with the charge neutralisation and the formation of secondary or tertiary aggregates from the primary ones, and then continues through the regular imbibition of water molecules round the completely or partially discharged colloidal aggregates, and finally ends into the formation of a jelly-mesh which entangles the whole of the dispersing phase. Most of these stages directly or indirectly depend on the valency of coagulating ions. It is difficult to find out the exact conditions of aggregation and still more difficult would be to assign quantitative relationships to the surficial and structural hydration. According to Rice,⁴ colloidal particles do not aggregate if $\frac{4\pi\sigma^2r}{D} > r_0^\infty$, where σ is the surface density of electric charge, r the thickness of the double layer, D the dielectric constant of the medium and r_0^∞ is the non-electrical surface tension of the colloid particle. Rice has also shown that aggregation will become very rapid when a definite σ is reached. The surface density of electric charge, σ , is bound to be effected by the adsorbed solvent layers round the partially discharged colloidal particle. The non-electrical surface tension of the colloidal particle in such cases would tend to merge into the surface tension of the solvent medium.

Experimental

We have carried experiments with different coagulating electrolytes, such as potassium chloride, potassium sulphate, potassium citrate, calcium chloride and barium chloride. The ferric phosphate sols were prepared by the usual Holmes method by adding potassium dihydrogen phosphate solution to a solution of ferric chloride in concentrations short of precipitation and dialysing the sol. The values of P and $\log R$ have been calculated from the observations given below.

Concentration of the sol = 62.92 g. ferric phosphate per litre. Purity of the sol $\text{Fe/Cl} = 0.3873/0.0765 = 5.06$. Amount of sol taken = 3 c.c. and the total volume = 5 c.c.

The above results have been summarised in Table II which show that the values of p and $\log R$ are not exactly the same and thus it is evident that ferric phosphate does not adsorb chloride, bromide and nitrate ions to the same extent, or these ions have some other more complicated preferential influence. The influence of different coagulating ions has been shown in Fig. 1.

TABLE I
With uni-univalent electrolytes

Conc of electrolyte used (C)	log C	Setting time, θ (secs)	log S (-log θ)	The values of p and log R calculated
<i>With 1.5 N-KCl</i>				
(1) 0.51 N	-0.2924	702	-2.8463	From (1) and (2)— $p=3.24$, log R = -1.90
(2) 0.33	-0.4815	2880	-3.4594	From (1) and (3)— $p=3.26$, log R = -1.89
(3) 0.27	-0.5686	5580	-3.7466	Mean value— $p=3.25$, log R = -1.90
<i>With N-KNO₃</i>				
(1) 0.40 N	-0.3979	4080	-3.6107	From (1) and (3)— $p=3.36$, log R = -2.27
(2) 0.38	-0.4202	4860	-3.6866	From (2) and (3)— $p=3.35$, log R = -2.28
(3) 0.33	-0.4815	7800	-3.8921	Mean value— $p=3.35$, log R = -2.28
<i>With 1.5 N-KBr</i>				
(1) 0.60 N	-0.2218	3960	-3.5977	From (1) and (3)— $p=2.75$, log R = -2.99
(2) 0.57	-0.2441	4560	-3.6590	From (2) and (3)— $p=2.75$, log R = -2.99
(3) 0.48	-0.3188	7320	-3.8645	Mean value— $p=2.75$, log R = -2.99

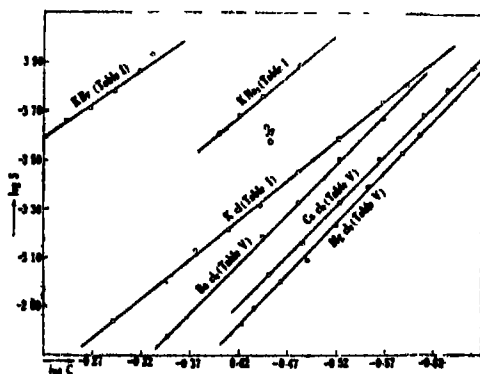


FIG 1 Influence of different coagulating ions

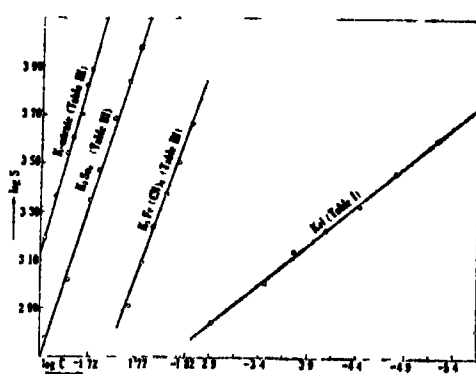


FIG 2 Influence of uni-polyvalent electrolytes

TABLE II

Electrolyte	p	log R
1.5 N-KCl	3.25	-1.90
N-KNO ₃	3.35	-2.28
1.5 N-KBr	2.75	-2.99

TABLE III
With uni-polyvalent electrolytes

Conc of electrolyte used (C)	log C	Setting time, θ (secs)	log S ($-\log \theta$)	The values of p and log R calculated
With N/10- K_2SO_4				
(1) 0.021 N	-1.6778	608	-2.7839	From (1) and (2)— $p=12.98$, log R=18.99
(2) 0.0186	-1.7305	2940	-3.4683	From (1) and (3)— $p=12.90$, log R=18.86
(3) 0.017	-1.7696	9300	-3.9685	Mean value— $p=12.94$, log R=18.93
With 0.0529 N-Potassium citrate				
(1) 0.02116 N	-1.6745	1560	-3.1931	From (1) and (3)— $p=14.67$, log R=21.37
(2) 0.02063	-1.6855	2280	-3.3579	From (2) and (4)— $p=14.66$, log R=21.35
(3) 0.01957	-1.7085	4920	-3.6920	Mean value— $p=14.66$, log R=21.36
(4) 0.01904	-1.7203	7380	-3.8681	
With 0.0455 N- $K_3Fe(CN)_6$				
(1) 0.01683 N	-1.7739	1252	-3.0976	From (1) and (2)— $p=11.27$, log R=16.89
(2) 0.01592	-1.7980	2340	-3.3692	From (1) and (3)— $p=11.29$, log R=16.93
(3) 0.01501	-1.8236	4560	-3.6590	Mean value— $p=11.28$, log R=16.91

The influence of uni-polyvalent electrolytes has been summarised in Table IV. In Fig. 2 are given the graphs showing the influence

TABLE IV

Electrolyte	p	log R
1.5 N-KCl	3.25	-1.90
N/10- K_2SO_4	12.94	18.93
0.0529 N-K-citrate	14.66	21.36
0.0455 N- $K_3Fe(CN)_6$	11.28	16.91

It is clear from these figures that the values of p and log R markedly increase if the jelly is formed by the uni-bivalent ion. The difference between uni-bivalent and uni-trivalent is not so marked as between uni-monovalent and uni-bivalent. The ferrocyanide ion does not fall into the series, probably due to the chemical reactivity with the iron sol.

TABLE V
With poly-univalent electrolytes

Conc of electrolyte used (C)	log C	Setting time, θ (secs)	log S ($-\log \theta$)	The values of p and log R calculated
<i>With 1.36 N-CaCl₂</i>				
(1) 0.3536 N	-0.4515	1104	-3.0429	From (1) and (3)— $p=4.06$, log R = -1.21
(2) 0.2992	-0.5240	2160	-3.3345	From (2) and (3)— $p=4.09$, log R = -1.19
(3) 0.2448	-0.6112	4920	-3.6920	Mean value— $p=4.07$, log R = -1.20
<i>With 1.5 N-BaCl₂</i>				
(1) 0.45 N	-0.3468	608	-2.7839	From (1) and (2)— $p=4.12$, log R = -1.35
(2) 0.30	-0.5229	3240	-3.5105	From (1) and (3)— $p=4.02$, log R = -1.39
(3) 0.27	-0.5686	4740	-3.6758	Mean value— $p=4.07$, log R = -1.37
<i>With 1.075 N-MgCl₂</i>				
(1) 0.3655 N	-0.4371	798	-2.9020	From (1) and (3)— $p=4.21$, log R = -1.06
(2) 0.3440	-0.4634	1020	-3.0086	From (2) and (3)— $p=4.23$, log R = -1.05
(3) 0.2472	-0.6069	4140	-3.6170	Mean value— $p=4.22$, log R = -1.05

The influence of poly-univalent electrolytes has been summarised in the following table

TABLE VI

Electrolyte	p	log R
1.5 N-KCl	3.25	-1.90
1.36 N-CaCl ₂	4.07	-1.20
1.5 N-BaCl ₂	4.07	-1.37
1.075 N-MgCl ₂	4.22	-1.05

As is expected, the values of p and log R do not much change with the valency of the positively charged ions as the sol itself is positively charged.

Discussion

From the above tables we see that in case of uni-univalent electrolytes such as potassium chloride, potassium nitrate and potassium bromide, the values of p and log R do show only a slight variation. The small differences are due to the specific nature of different ions which are not adsorbed by ferric phosphate to the same extent. The uni-polyvalent electrolytes as potassium chloride, potassium sulphate and potassium citrate show a marked change

in the values of p and $\log R$, while in the case of potassium ferricyanide, the values of these constants lie between those for potassium chloride and potassium sulphate. It seems that this is due to the chemical reaction taking place between the sol and the electrolyte as it is evident from the change of colour exhibited during gelation. The gelation of ferric phosphate sol qualitatively obeys the Schulze-Hardy law. The behaviour of poly-univalent electrolytes as calcium chloride, barium chloride and magnesium chloride is practically the same and the values of p and $\log R$ do not show much change. The constants in the case of poly-univalent electrolytes are a little higher than in the case of uni-univalent electrolytes.

The jelly formation of ferric phosphate sol in this respect closely resembles the coagulation of positively charged ferric hydroxide sol. It is interesting to note that the results obtained by Freundlich, Weiser and Dhar on positively charged ferric hydroxide sol are in fair agreement with ours. From Freundlich's observations,⁵ the order of precipitating power of the anions is dichromate > sulphate > hydroxide > benzoate > chloride > nitrate > bromide > iodide. Dhar⁶ has obtained from this sol the following series

Ferricyanide > citrate > oxalate > sulphate > hydroxide > nitrate > chloride

No work has been done in this line on the coagulation of ferric phosphate and arsenate sols, but it is expected that these sols would also behave similarly. We have shown that gelation is also essentially a coagulation process and therefore, similar results are expected in gelation too. From the results recorded in the previous tables, the values of $\log R$ are in the following order.

With anions citrate > sulphate > ferricyanide* > chloride > nitrate > bromide

With cations magnesium > calcium > barium > potassium. The values of p are in the following order for the ferric phosphate sol

K-citrate > K_2SO_4 > $K_3Fe(CN)_6$ > $MgCl_2$ > $BaCl_2$ > $CaCl_2$ > KNO_3 > KCl > KBr . The difference in the value of p is very much marked only when we proceed from KCl to K_2SO_4 or to K-citrate, while in other cases the values are almost the same.

By coagulating or flocculating power is usually meant the concentration of electrolyte (expressed in moles or millimoles per litre) necessary to precipitate the sol completely in a stated time. The gelation power of an electrolyte can also be similarly defined in terms of the concentration of electrolyte necessary to set the sol to a gel in a stated time. In order to set a sol in

* Anomalous due to chemical reaction

time S , let the concentration of the monovalent electrolyte be C_1 , so that

$$S = \log R + p \log C_1$$

The sol with the same characteristics, p and R , would require the concentration C_2 to set the sol to a jelly in the same time S with the polyvalent electrolyte. If the two concentrations are related according to Whetham or some other general law so that $C_1 = \alpha C_2^r$, where r denotes some power depending upon the valency of the ion, the gelation time S would be given by

$$S = \log R + p \log (\alpha C_2^r)$$

$$\text{or} \quad S = \log R + p \log \alpha + r p \log C_2$$

Thus the constant $\log R$ is replaced by another constant $\log R + p \log \alpha$ and the constant p is replaced by another constant $r p$. The variations observed in the values of $\log R$ and p when gelation is affected with different ions as recorded in the previous tables qualitatively agree with these assumptions. The quantitative differences are due to the influence of the similarly charged ions, different adsorbabilities and other factors which do not make the results exactly comparative.

Summary

In continuation with the previous work, the authors have studied the influence of different coagulating ions on the setting of ferric phosphate gels. The values of p , the jelly characteristic and R the rate constant in the equation $\log S = \log R + p \log C$ do not change much with uni-univalent electrolytes. The slight variations with chloride, bromide and nitrate ions are due to the different adsorbabilities of these ions by ferric phosphate. When the jelly formation is affected with uni-polyvalent ions the marked variations are observed consistent with Whetham's law, or any other generalized expression. With poly-univalent electrolytes, the values of p and $\log R$ do not markedly change as the sol itself is positively charged.

In the end, the authors are grateful to Prof. N. R. Dhar for his interest throughout the work.

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MAGNETISM OF STRONTIUM

BY DR S RAMACHANDRA RAO AND MISS K SAVITHRI

(Annamalai University, Annamalai Nagar)

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1 Introduction

A COMPREHENSIVE survey of the magnetic properties of elements was first carried out by Honda (1910) and Owen (1912). The magnetic susceptibilities of nearly sixty elements were measured at temperatures ranging from that of liquid air to about 1200° C. These important investigations have been supplemented by those of later workers. The results of these observers have formed the basis for theoretical investigations on the properties of metals and non-metals.

A metal may be considered to be built up of a lattice of metallic ions, the remaining electrons of the individual atoms being considered free or partly bound in accordance with their energy values. Pauli (1927) considered these electrons to constitute an electron gas and deduced the following expression for the paramagnetic susceptibility $(\chi_A)_e$ of such electrons in a gram atom of the metal

$$(\chi_A)_e \times 10^6 = 48.17 \, q/V_0$$

where q is the number of free electrons per atom and V_0 the width in volts of the energy band occupied by the electrons in the completely degenerate state. Landau (1930) and others showed that the curvature of the paths of the free electrons in a magnetic field would be associated with a diamagnetic susceptibility numerically equal to one-third of the paramagnetic susceptibility. This gives for $(\chi_A)_e$ the expression,

$$(\chi_A)_e = 32.11 \times \frac{q}{V_0}$$

For perfectly free electrons, V_0 is of the order of several volts. The effect of the periodic potential field due to the lattice ions will be to narrow the bands but the above equation will still be applicable as an approximation. The diamagnetism of bound electrons has been discussed by Peierls (1933). When the atom has only one loosely bound electron, only one band is to be considered. This is found to be the case with the alkali metals. The narrower the band, the greater will be the number of quantum states per unit energy range and the larger the paramagnetism. In the case of the alkaline earth

elements, an overlapping of the bands due to the two valence electrons should occur, since otherwise the solid would be non-conducting. The greater the overlap, the larger will be the paramagnetism.

The electrons in the closed groups in the atoms will give rise to a normal diamagnetic effect. The gram atomic susceptibility χ_A of the element is the sum of $(\chi_A)_i$, the susceptibility per gram atom of the ion and $(\chi_A)_e$.

The magnetic susceptibilities of calcium, strontium and barium were first determined by Owen (1912). He obtained for the specific susceptibility of these elements the values of $+1.10$, -0.2 and $+0.93$ *. The metals used in Owen's investigations had a fairly large iron content. To allow for such ferromagnetic impurity, the susceptibility of an element was determined at different field strengths. The specific susceptibility χ_p of the pure specimen could be represented by the expression $\chi_p = \chi_i + \frac{\sigma_m}{H}$ where χ_i is the specific susceptibility of the impure element, σ the specific intensity of magnetization of the ferromagnetic impurity, m the mass of this impurity present in a gram of the substance and H the intensity of the magnetic field. Honda and Owen drew for every element investigated, a graph between χ_i and H . By extrapolating this graph, the value of the specific susceptibility at infinite field strength was determined. This value gave the corrected specific susceptibility χ_p .

If the iron content in a substance is negligibly small, the χ , H graph will be very nearly parallel to the axis of H . Owen's results for calcium, strontium and barium show a very large ferromagnetic content, the χ , H graphs being very steep. Hence the specific susceptibility values obtained by extrapolating such graphs are likely to be vitiated by errors of extrapolation. Owen's results show that whereas calcium and barium are paramagnetic, strontium appears exceptional in being diamagnetic. Two specimens of strontium were studied by Owen, the range of field-strength being from about 13 to 26 kilogauss. The specific susceptibility for one of the specimens varied from about $+6.4$ to about $+3.4$ in the above mentioned range of field strength. In the case of the other specimen this variation was from $+2.7$ to $+1.2$. Thus the observed specific susceptibilities of strontium were all paramagnetic.

Stoner (1934) drew attention to the possibility of an overcorrection for the relatively large iron content, resulting in a diamagnetic value for strontium. The present investigation was undertaken with a view to examine this problem. A careful thermomagnetic examination of strontium has also

* All susceptibility values in this paper are given in 10^{-8} unit.

been made Owen studied the specific susceptibility of this element at different temperatures ranging from about -160°C to $+15^{\circ}\text{C}$ and found no variation in this temperature range But the susceptibility of the specimen was about $+8$ and measurements seem to have been made at different temperatures only at one field strength

Lane (1933) studied the specific susceptibility of barium in the range of temperatures 20°C to 400°C The value increased from $+0.145$ at 20°C to $+0.415$ at 400°C A slight discontinuity in the χ, T curve at about 350°C . was observed A change of slope of the curve connecting electrical resistance and temperature is also found at about 350°C This result may be explained if it is assumed that the top of the Fermi distribution occurs in a region where the bands corresponding to the two valence electrons overlap

2 Experiment

The metal available was a pure specimen of strontium from Merck A spectroscopic analysis showed the presence of traces of calcium and lead A chemical examination was made by dissolving a known weight of strontium in hydrochloric acid and precipitating the sulphate The purity of the specimen was found to be not less than 99.8%

The specific susceptibility of strontium was determined by the Curie method Small bulbs containing 20 to 60 mg of strontium were prepared in the following manner A pyrex glass tube having a diameter of about 5 mm was blown to have the shape shown in Fig 1 After thoroughly cleaning and drying the tube, a suitable quantity of strontium was introduced into the tube The end A was connected to a high vacuum equipment and the pressure brought down to 10^{-4} cm of mercury The tube AE was warmed with a bunsen burner in order that traces of paraffin oil (into which the given specimen of strontium was immersed) might evaporate away The metal above the constriction at B was then heated by a blow-pipe flame. By jerking the tube vigorously, the molten metal was made to pass through the constrictions B and D into the spherical bulb E Any oxide film on the metal was removed by the constrictions The metal which collected in E possessed a bright metallic lustre The tube was finally sealed off at D, the molten glass being drawn into the form of a hook to enable the bulb E to be suspended during the magnetic measurements.

The electromagnet used was a large one of the Pye type. The pole-pieces of diameter 5 cm were kept suitably inclined to give rise to a non-uniform field The electromagnet was capable of carrying a current of about 15 amperes. Since the maximum current used in the present investigation

was only 6 amperes the heating of the coils was very little. The currents were measured with an ammeter of the Cambridge Scientific Company, reading accurately to 0.05 ampere and by estimation to 0.005 ampere. The deflections were read by a lamp and scale arrangement.

The retorsion method was adopted. In the presence of the magnetic field the bulb containing the specimen under investigation was brought to the same position as could be judged by the spot of light on the scale.

The standard substance used was water, the specific susceptibility of which was assumed to be -0.72 at 30°C .

The bulbs were weighed with a Sauter's balance correctly to within 0.1 mg. After the magnetic experiments, the bulbs were broken open. The metal was dissolved in dilute nitric acid. The magnetic deflections corresponding to the bulbs were then determined after drying them in a vacuum desiccator for a day. The masses of the metal specimens varied from 20 to 60 mg.

It may be shown that if d_s and d_w are the deflections produced by masses m_s and m_w of strontium and water respectively

$$\frac{d_s}{d_w} = \frac{m_s \chi_s - k_a v_s}{m_w \chi_w - k_a v_w}$$

where χ_s and χ_w are the specific susceptibilities of strontium and water respectively, k_a is the volume susceptibility of air at the room temperature and v_s and v_w are the internal volumes of the metal and water bulbs.

During the determination of the specific susceptibility of strontium at high temperatures, the volume susceptibility k_T of air at any absolute temperature T was determined from the relation $k_T/T^2 = \text{a constant}$. The volume susceptibility of air at N.T.P. was assumed to be $+0.029$ *.

3 Results

The results obtained with 9 specimens are given in Table I.

The values of the specific susceptibility at different field currents are given in column 4. The last column gives the specific susceptibility of the metal obtained by drawing χ , $1/H$ graph and extrapolating it to infinite field strength. The average specific susceptibility of strontium is found to be $+1.05 \pm 0.03$. The element is thus found to be paramagnetic, contrary to the observations of Owen (1912) who obtained the value of -0.2 for the metal. The gram atomic susceptibility of the metal is therefore $+92.0$.

The specific susceptibility of strontium was determined at different temperatures ranging from 0 to 260°C . The bulb containing strontium was

* *Int Crit Tables*, 1929, 6, 354

TABLE I

Bulb No	Mass (mg)	Current (amperes)	X	X (extrapolated)
1	28.7	2 3 4 5	5.15 3.42 2.34 2.10	1.02
2	42.9	2 3 4 5 6	4.14 2.75 2.11 1.84 1.76	1.02
3	34.5	2 3 4 5	3.62 2.50 1.81 1.69	1.03
4	54.5	2 3 4 5	3.41 2.35 1.78 1.63	1.02
5	64.8	2 3 4 5 6	2.80 2.00 1.63 1.51 1.42	1.08
6	40.6	2 3 4 5	2.02 1.61 1.38 1.35	1.08
7	51.8	2 3 4 5	1.91 1.53 1.38 1.32	1.06
8	56.3	2 3 4	1.64 1.35 1.25	1.06
9	61.0	2 3 4 5	1.83 1.50 1.33 1.24	1.06

heated by enclosing it inside an electric heater made by winding constantan wire on an asbestos cylinder. The pole pieces were cooled by cotton wads drenched with iced water. The magnetic field inside the heater was in no way disturbed by the heating coils.

A preliminary investigation was carried out by enclosing inside the heater a thermometer, reading to 340° C and one junction of a thermo-electric couple made of silver and constantan wires. The terminals of the thermo-couple

were connected to a sensitive pointer galvanometer. A graph was drawn between the reading of the galvanometer and the corresponding thermometer reading, by gradually increasing the temperature inside the heater. During the magnetic experiments, the temperature of the heater was determined by using the thermocouple. Test experiments showed that temperatures measured in this manner were accurate to within 5° . The specific susceptibility at the temperature of melting ice was determined by enclosing the specimen within a chamber cooled outside by melting ice.

The variation with temperature of the susceptibility of the pyrex glass containers was studied separately. The bulbs were found to possess a diamagnetic susceptibility which was constant in the temperature range investigated.

Fig. 2 shows the graph drawn between the specific susceptibility of strontium and temperature. The specific susceptibility is found to increase from 1.02 at 0°C to about 1.09 at 65°C . Thereafter the susceptibility decreases gradually to about 0.73 at 260°C .

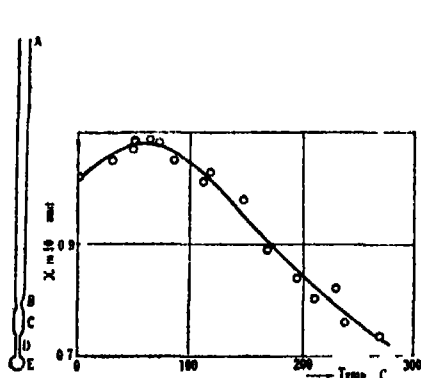


FIG. 1

FIG. 2

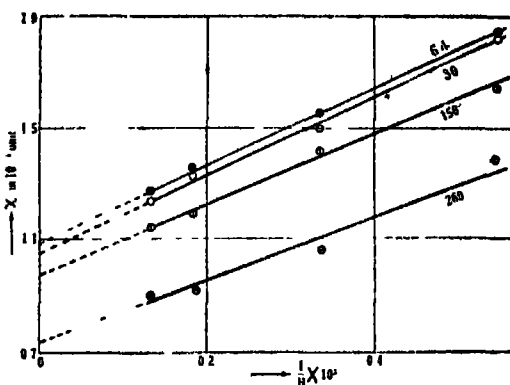


FIG. 3

Fig. 3 shows the graphs between χ and $1/H$ at temperatures of 30° , 64° , 150° and 260°C . These graphs are presented to show how χ varies with $1/H$ in the different ranges of temperatures studied. The slope of the straight line graphs is found to decrease appreciably at higher temperatures. One would expect this to take place in view of the decreasing intensity of magnetization of the ferromagnetic impurity at the higher temperatures.

4 Discussion

The gram atomic susceptibility of the metal is found to be +92.0. If the ionic susceptibility of Sr^{+2} is assumed to be -15.6 after Kido (1933), we obtain for the contribution to the susceptibility $(\chi_A)_i$ of a gram atom of the

metal by the valence electrons (2 per atom) the value of + 107.6. From the equation

$$(\chi_A)_e = \frac{32}{V} \frac{1}{q}$$

where $q = 2$ for the strontium atom, V is found to be 0.6 volt. This measures the width of the occupied energy range in the completely degenerate state of the valence electrons in the metal. This result supports the observation of Stoner (1934) that in the alkaline earth elements, the electron energy bands are much narrower than for free electrons. Our observation brings strontium in a line with calcium and barium so far as their magnetic properties are concerned.

The temperature variation of the specific susceptibility of strontium seems to be of special interest. Considering the Fermi energy distribution of the two overlapping bands, the high value of the specific susceptibility of strontium indicates that the overlapping of the bands must be considerable. The temperature coefficient of susceptibility of a divalent element has been shown (Stoner, 1936) to be dependent in a critical manner upon the relation between $\nu(\epsilon)$ the number of states per unit energy range and the energy ϵ of the overlapping bands. It would be of interest to apply these considerations to strontium in the light of the results explained above.

In magnetic properties, strontium seems to behave like the rare earth elements. It has a comparatively high paramagnetism. A clear account of the spin paramagnetism of the rare earths is given by Wilson (1939, 69). In the absence of a magnetic field, the number of free electrons with their spins along the direction of the field is equal to the number with their spins in the opposite direction. The effect of the magnetic field H is to increase the former and decrease the latter. The reversal of spin increases the kinetic energy of such electrons which go into higher energy states which were unoccupied. It is found therefore that the electrons near the top of the Fermi distribution really contribute to the paramagnetism in these cases.

Stoner (1936a) has derived the following formula for $(\chi_A)_e$, the electronic contribution to the gram atomic susceptibility

$$(\chi_A)_e \times 10^6 = 64.21 n(V_0) \left[1 + 1.222 \times 10^{-8} T^2 \left\{ \frac{1}{n} \frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n} \frac{\partial n}{\partial V} \right)^2 \right\}_{V=V_0} \right]$$

Here $n(V)$ is the number of states for one direction of spin per atom per volt, T is the absolute temperature and V_0 is the maximum Fermi energy in volts.

The spin susceptibility will increase or decrease with temperature in the low temperature range as the sign of the quantity

$$\left\{ \frac{1}{n} \frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n} \frac{\partial n}{\partial V} \right)^2 \right\}_{V=V_0}$$

is positive or negative. If instead of in volts, the energy is expressed in ergs, the above expression changes to

$$\left\{ \frac{1}{n} \frac{\partial^2 n}{\partial \epsilon^2} - \left(\frac{1}{n} \frac{\partial n}{\partial \epsilon} \right)^2 \right\}_{\epsilon=\epsilon_0}$$

It may be shown that the temperature coefficient of the susceptibility due to electrons in an isolated band will be negative. For in the above expression, the first term may be shown to be negative in such cases and the second term is negative or zero.

When there is overlapping of two bands as in the case of the alkaline earth elements, the sign of the temperature coefficient of susceptibility will depend on the extent of overlapping. The high paramagnetism of strontium shows that this overlapping must be considerable. It is of interest that in exactly such a case the temperature coefficient of the paramagnetism due to electrons assumes importance. The variation of $n(\epsilon)$ as a function of ϵ when the bands overlap considerably may be such that $\frac{\partial^2 n}{\partial \epsilon^2}$ may be positive and sufficiently large when $\epsilon = \epsilon_0$, the maximum Fermi energy. In this case a positive temperature coefficient will be obtained. The positive temperature coefficient obtained by Lane (1933) for the paramagnetic susceptibility of barium could be generally explained on this basis. But the increase is so large that a satisfactory quantitative explanation on these lines could not be given.

If increase of temperature brings about directly or indirectly a displacement of the second band relatively to the other reducing the extent of overlapping, the temperature coefficient may change over from a positive to a negative value. At very large temperatures, the susceptibility should decrease with T for, when the electron behaves classically, we have the volume susceptibility K varying as T^{-1} .

The question arises whether the relative displacement of the second band at temperatures within 100°C could be brought about directly by temperature variation or by changes in physical properties resulting from the elevation of temperature. Unfortunately data relating to strontium are very meagre and no definite indication is available under this head.

However, mention may be made of the investigations of Bridgman who studied the electrical resistance of calcium and strontium at 0°, 50° and 100° C at different pressures. The pressure coefficient of calcium was found to increase with rising temperature. That of strontium decreased very slightly at 0° C with rise of pressure, but at 50° C, it increased with rise of pressure to 2000–3000 kilograms per sq cm then showed a flat maximum and then decreased. At 100° C the behaviour was like that at 50° except that the maximum was sharper, Mellor (1923, 636). These results show that the behaviour of strontium at 0° C is different from that at 50° C.

Summary

The specific magnetic susceptibility of strontium has been determined by the Curie method. The value at 30° C is found to be $+1.05 \times 10^{-6}$. A thermomagnetic investigation of the metal showed the specific susceptibility to increase from 1.02×10^{-6} at 0° C to 1.09×10^{-6} at about 65° C. The susceptibility decreased thereafter to $+0.73 \times 10^{-6}$ at 260° C. Attention is drawn to the interest which these observations have in the light of the Fermi distribution of energy of the valence electrons of strontium.

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RAMAN EFFECT AND HYDROGEN BONDS

Part I. Mixtures of Esters and Acceptor Molecules

BY G V L N MURTY AND T R SESHADRI

(From the Department of Chemistry, Andhra University, Waltair)

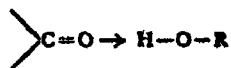
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THE hydrogen bond or the binding of two atoms by means of an atom of hydrogen has been successfully employed to give concreteness to such indefinite terms as partial valence, secondary forces, co-ordination, association and ortho-effect. Such a role of hydrogen (secondary forces) seems to have been first postulated by Moore and Winmill¹ to account for the differences in strength between tertiary and quaternary ammonium bases. The idea was developed into 'the hydrogen bond' within the scope of Lewis valence theory by Huggins² and Latimer and Rodebush³ to account for the association of water and for the formation of ions such as HF_2^- . It was extended to organic compounds with special reference to chelate structures by Sidgwick,⁴ who considered it as a particular case of Werner's co-ordination theory. This concept of hydrogen bond implies the capacity of hydrogen to assume a co-valency of two. Association between two molecules is represented as $-\text{A}-\text{H}-\text{A}'-$ where A and A' are the electronegative atoms of the two molecules which the 'H' atom holds together. The physical objections to this idea of co-valency of two for hydrogen, which implies a group of four shared electrons are very strong. The difficulties, however, seem to have been overcome by introducing the idea of resonance⁵ between two structures in the first of which the 'H' atom is attached to one and in the second to the other of the two atoms which it holds together ($\text{R}-\text{H}-\text{R}'$, $\text{R}'-\text{H}-\text{R}$). Whatever may be the exact details regarding the mechanism of the hydrogen bond, its occurrence is beyond doubt and there is good evidence for the capacity of a hydrogen atom to hold two other atoms together.

Newer methods of investigation have provided extensive experimental material which supports the theory of hydrogen bonds in a remarkable manner. The importance of this subject and the interest evinced by workers in various fields of investigation is clearly indicated by the recent discussions of the Faraday Society.⁶ Studies on the crystal structure of both inorganic and organic compounds have revealed several features indicating the existence of hydrogen bonds. The work of Pauling and Brockway,⁷ employing the method of electron diffraction, has definitely established the existence

of dimers of carboxylic acids involving hydrogen bonds. But by far the most important contribution to our knowledge of the subject has been made by the investigations of infra-red absorption spectra. Wulf and collaborators⁸ have examined the spectra of many organic compounds in solution and noticed the absence of the second harmonic of the OH band in cases where hydrogen bonds were to be anticipated. An account of similar work turned out in Cotton's laboratories in Paris since 1932 is given by Freyman.⁹ Buswell, Dietz and Rodebush¹⁰ investigated a large number of compounds using the region of the fundamental hydroxyl band and found the important generalisation that the presence of hydrogen bonds is accompanied by a considerable increase in the absorption and a marked change in the frequency of the band, the shift being in the direction of longer wavelengths. This work has been confirmed by other investigators¹¹ independently. Walter Gordy and co-workers¹² have made an extensive series of investigations on liquids and binary liquid mixtures and thus obtained information regarding the formation of hydrogen bonds between similar as well as dissimilar molecules. No attempt has, however, been made in this paper to give any exhaustive account of the infra-red studies; only items relevant to the discussion on Raman effect and hydrogen bonds have been included.

In regard to the application of the Raman effect to the study of hydrogen bonds no systematic investigation has so far been reported, though the concept has been utilised by some workers¹³ in the past to explain certain peculiarities in the Raman spectra of compounds and binary mixtures observed by them. Since the potentialities of this method are obviously great, the investigations described in this series of communications have been undertaken. The usual procedure adopted in infra-red spectroscopy is to determine the effect of hydrogen bond formation on the absorption of the group which carries the hydrogen, as for example the OH group of alcohols and phenol. It is relatively in very few cases that the effects of the bond on the second group involved, such as the C=O in carbonyl compounds, have been examined. The large amount of data obtained from infra-red studies seems to indicate that hydrogen bond formation is more or less universal in liquids and liquid mixtures of molecules having donor and acceptor atoms. In our investigations attention is confined to cases of hydrogen bond formation where the oxygen of the C=O group of various carbonyl compounds acts as the donor. Such cases may be represented as below —



It readily follows that there should be a weakening of the C=O bond resulting in a lowering of the frequency of the line attributable to this linkage.

In this procedure possibilities of accuracy and definiteness are greater since the Raman line of the $C=O$ is usually bright and sharp and any modifications undergone by it can be easily recorded. On the other hand the utilisation of the OH group is difficult for two reasons, viz, (i) the difficulty of recording the OH band and (ii) the non-existence of any hydroxylic compound devoid of hydrogen bond in it for use as the correct standard.

Hydrogen bonds can be classified broadly under two heads namely, intermolecular and intramolecular hydrogen bonds. In the former, the two atoms linked by the hydrogen belong to different molecules whereas in the latter they are present in the same molecule. Intermolecular hydrogen bonds may further be subdivided as the homo- and the hetero-molecular types according as the union is brought about between similar and dissimilar molecules respectively. These bonds are represented by many American workers by means of dotted lines joining the donor atom and the hydrogen. It seems to be more reasonable to represent them by means of arrows pointing in the direction of the pull of electrons as $>C=O \rightarrow H-O-R$. The terms donor and acceptor are used by some¹⁴ in connection with the proton but it appears to be more correct to refer them to the electrons since, according to the ideas advanced by Sidgwick,⁵ it is only the electrons that change their positions in the resonance condition. Further, this will be in accordance with the accepted usage of these terms in connection with co-ordinate valency.

The essential requisites for the formation of hydrogen bonds are (i) the existence of 'H' atoms with the capacity to serve as acceptors and (ii) the presence of atoms having free pairs of electrons, enabling them to act as donors. As examples may be mentioned 'H' atoms present in hydroxylic and amino compounds under category (i) and oxygen, nitrogen and chlorine atoms under category (ii). Consequently the strength of hydrogen bonds will depend upon the anionoid power of the donor and the cationoid power of the acceptor atoms and a large variation in bond strength is possible.

In this connection it may be recalled that Bernal¹⁵ proposed to distinguish between two types of hydrogen bonds and to call them the hydrogen and the hydroxyl bonds respectively. "In the hydrogen bond the hydrogen atom is attached with almost equal firmness to the two oxygen atoms which it joins, the $O-H \cdots O$ distance being $2.50-2.65 \text{ \AA}$ corresponding to an energy of the bond of about 8000 cal/mol . The $O-H$ links in these conditions are greatly weakened and the characteristic OH band is not found in the normal spectral region. In the 'hydroxyl bond' the hydrogen atom is still regarded as belonging to its parent oxygen, although the $O-H$ link is somewhat weakened

and the band is observed at a lower frequency. The distance $O-H \cdots O$ in this type of bond is taken to be 2.7 to 2.9 Å and the energy involved about 5,000 cal/mol. Venkateswaran¹⁶ in the course of his work on the Raman spectra of some inorganic acids came to the conclusion that, in view of the fact that the hydrogen bonds are capable of exhibiting varying bond strengths, the distinction between the two types as proposed by Bernal is too artificial.

With a view to test the validity of the generalisation namely 'the anionoid power of the donor atoms and the cationoid power of the acceptor atoms determine the strength of hydrogen bonds' and to examine the need for division into different categories as proposed by Bernal, a large number of organic compounds containing $C=O$ groups of different types and mixtures of these with phenol, alcohol, and chloroform have been investigated. Incidentally it was expected that the results would supplement data obtained from the study of infra-red spectra.

The experimental methods are essentially the same as those described by us in our former publications in these *Proceedings*. In this part the results of investigation of the Raman spectra of various esters and their mixtures with acceptors like phenol, methyl alcohol, ethyl alcohol and chloroform are dealt with. The following esters have been employed:

(1) Ethyl acetate, (2) Ethyl benzoate, (3) Ethyl cinnamate, (4) Phenyl acetate, (5) Phenyl propionate, (6) Phenyl benzoate, (7) Phenyl cinnamate and (8) Benzyl-acetate. In addition to the above, coumarin has been also included in this part because, as shown by us previously it behaves very much like a phenyl ester.¹⁷

Pure substances were available in most cases and they were further purified by repeated distillation or crystallisation. High boiling liquids were as a rule distilled under reduced pressure. Phenyl propionate was prepared by heating dry phenol with sodium propionate and propionic anhydride at 160° C in an oil bath for six hours. It was repeatedly washed with sodium carbonate solution, ether extracted, dried over anhydrous calcium chloride and distilled under reduced pressure after the ether had been driven off. Phenyl cinnamate was prepared by the action of phenol on cinnamoyl chloride in the presence of pyridine. It was recrystallised several times from alcohol. Phenol was dried over calcium chloride and distilled perfectly out of contact with air and moisture and fresh samples were employed, because on keeping, it acquires a reddish colour which is likely to absorb much of the exciting radiation, viz., 4358 Å. Methyl and ethyl alcohols were purified by distillation over calcium turnings. Chloroform was subjected to slow distillation.

A description of the spectra of the substances as recorded by us is given below and subsequently the effects of mixing the esters and the acceptor solvents on the carbonyl frequencies are dealt with. No attempt is made to give any exhaustive list of references to the previous work on the Raman Spectra of the substances because they could easily be obtained from the recent book published by Hibben¹⁸. However, select references relevant to the discussions are given in proper places.

Spectra of the Donor Substances in the Pure State

(Figures within brackets indicate visual estimates of the relative intensities)

(1) *Ethyl acetate*—376 (9) 633 (9) 784 (3) 846 (10) 916 (1) 938 (1) 999 (1) 1045 (2) 1096 (1) 1114 (3) 1452 (6*b*) 1739 (6*b*) 2880 (1) 2940 (8*b*) 2982 (7*b*)

(2) *Ethyl benzoate*—193 (3) 214 (2) 326 (4) 395 (1) 488 (1) 588 (1) 619 (6) 677 (4) 783 (2) 809 (2) 852 (5) 1004 (10) 1029 (3) 1112 (3) 1160 (2) 1178 (2) 1277 (5) 1314 (2) 1371 (2) 1381 (2) 1453 (3) 1493 (1) 1602 (10) 1720 (8) 2935 (2) 2972 (2) 3076 (6)

(3) *Ethyl cinnamate*—274 (1) 357 (1) 580 (1) 618 (1) 715 (2) 840 (2) 945 (2) 974 (2) 1000 (7) 1030 (3) 1153 (2) 1180 (4) 1202 (6) 1255 (2) 130 (1) 1450 (2) 1578 (2) 1598 (7) 1634 (10) 1712 (5*b*) 2940 (1) 3066 (1)

(4) *Phenyl acetate*—185 (1) 239 (4) 272 (4) 341 (1) 529 (5) 597 (1) 618 (4) 664 (4) 694 (2) 744 (5) 815 (5) 829 (1) 892 (2) 926 (1) 1004 (10) 1027 (3) 1079 (1) 1163 (6) 1195 (6) 1262 (1) 1311 (1) 1369 (1) 1429 (1) 1448 (1) 1596 (8) 1766 (3) 2912 (2) 3047 (2) 3070 (7)

(5) *Phenyl propionate*—186 (1) 230 (2) 268 (2) 338 (1) 529 (3) 618 (2) 660 (2) 740 (3) 820 (4) 890 (0) 926 (0) 1004 (10) 1030 (2) 1163 (3) 1195 (3) 1598 (6) 1760 (3) 2912 (1) 3072 (5)

(6) *Phenyl benzoate*—340 (3) 610 (3) 674 (1) 850 (2) 1000 (10) 1030 (2) 1115 (2) 1158 (2) 1176 (1) 1274 (3) 1310 (1) 1365 (1) 1450 (2) 1604 (10) 1740 (7) 2930 (1) 3070 (5)

(7) *Phenyl cinnamate*.—(The spectrum was studied in solution in carbon tetrachloride.)

274 (1) 375 (1) 580 (1) 618 (1) 715 (2) 840 (2) 945 (2) 974 (2) 1000 (7) 1030 (3) 1153 (2) 1180 (4) 1202 (6) 1255 (2) 1301 (1) 1450 (2) 1540 (2) 1570 (2) 1596 (7) 1633 (10) 1742 (4) 2940 (1) 3067 (1).

(8) *Benzyl acetate*.—187 (2) 223 (2) 263 (1) 300 (1) 329 (1) 426 (0) 499 (1) 580 (5) 619 (3) 642 (2) 751 (5) 820 (1) 839 (3) 919 (2) 1002 (10) 1028 (4)

1077 (3) 1119 (3) 1157 (3) 1181 (2) 1213 (1) 1244 (1) 1263 (2) 1452 (2) 1585 (2)
1606 (8) 1745 (4) 2940 (2) 3070 (7)

(9) *Coumarin* —(a) Solution in carbon tetrachloride, Frequencies between 1000–2000 cm^{-1} are given below —

1030 (1) 1102 (3) 1125 (3) 1158 (3) 1178 (10) 1228 (4) 1257 (2) 1330 (4)
1457 (2) 1492 (2) 1570 (8) 1610 (6) 1625 (6) 1742 (6)

(b) Pure solid melted and resolidified —1030 (1) 1100 (3) 1128 (3)
1156 (3) 1181 (10) 1228 (4) 1260 (4) 1328 (6) 1457 (2) 1486 (4) 1567 (8)
1604 (6) 1620 (6) 1708 (6) 1731 (6)

Spectra of Acceptor Substances

(1) *Phenol* —236 (3) 532 (1) 624 (2) 750 (1) 812 (1) 826 (1) 1000 (10)
1028 (6) 1070 (0) 1158 (2) 1167 (3) 1255 (1) 1595 (5) 1601 (5) 3014 (0) 3046 (3)
3060 (10)

(2) *Ethyl alcohol* —434 (1) 880 (6) 1051 (3) 1095 (3) 1453 (5) 2875 (5)
2930 (10) 2972 (4)

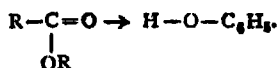
(3) *Methyl alcohol* —1030 (4) 1464 (5) 2838 (5) 2945 (6)

(4) *Chloroform* —264 (5) 367 (5) 688 (10) 765 (5b) 1220 (1)

In general the esters were mixed with the solvents in the proportion, 1:1 and the spectra of the mixtures compared with those of the pure substances. When solids like coumarin and phenol were concerned the two molten substances were mixed and the Raman tube containing the molten mixture was kept at about 80° C by means of an electric heater. In many cases it was observed that the spectra of the mixtures showed conspicuous changes as far as the C=O frequency was concerned.

Mixtures of Esters with Phenol

The results obtained with these mixtures are presented in Table I. The most striking effects are noticed here, in all cases new C=O lines which are bright make their appearance and these are attributable to hydrogen bond formation as represented below —



Except the case of coumarin mixture, in which the original C=O frequency has completely disappeared, the others continue to exhibit the unchanged frequencies of the esters with considerably diminished intensity. Obviously the mixtures contain a portion at least of the uncombined esters. The larger

TABLE I

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with phenols	Difference
Ethyl acetate	1739	1700, 1739	39
Ethyl benzoate	1720	1695, 1720	25
Ethyl cinnamate	1712	1685, 1712	27
Phenyl acetate	1766	1716, 1766	50
Phenyl propionate	1760	1710, 1760	50
Phenyl benzoate	1740	1704, 1740	36
Benzyl acetate	1745	1715, 1745	30
Coumarin	1742 (in CCl ₄)	1710	32

shifts are noticed with esters having high C = O frequencies and *vice-versa*, the range in the values lies between 50 and 25 wave numbers

Ester Alcohol Mixtures

Anhydrous ethyl and methyl alcohols were employed and it was noticed that the two gave identical results as far the C = O frequency shift was concerned. Here also coumarin mixtures gave a new C = O frequency, the original one having disappeared. In regard to the others the effects are not so prominent as in the case of phenol. The results are presented in Table II and the changes are attributed to the formation of hydrogen bonds of the following type

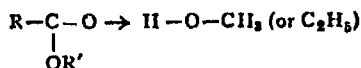


TABLE II

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with alcohol
Ethyl acetate	1739	diffuse
Ethyl benzoate	1720	1722
Ethyl cinnamate	1712	1712
Phenyl acetate	1766	1746, 1766
Phenyl cinnamate	1742	diffuse
Coumarin	1742 (in CCl ₄)	1720

Diffuseness of the lines mentioned above is towards shorter wavelengths and does not exceed 15 wave numbers

Ester-Chloroform Mixtures

The tendency to form hydrogen bonds is, in general, as weak as in the case of the alcohol mixtures as will be evident from Table III.

However, coumarin, phenyl cinnamate and phenyl acetate exhibit marked shifts in the C=O frequencies even here due to complex formation as below

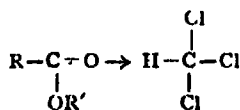


TABLE III

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with chloroform
Ethyl acetate	1739	1736
Ethyl benzoate	1720	1722
Ethyl cinnamate	1712	diffuse
Phenyl acetate	1766	1746, 1766
Phenyl benzoate	1740	diffuse
Phenyl cinnamate	1740	1722
Benzyl acetate	1745	1740
Coumarin	1742 (in CCl ₄)	1720

Diffuseness of the lines mentioned above is towards shorter wavelengths and does not exceed 15 wave numbers.

All the observed results may be consolidated and classified as follows:—

(i) Those in which a shift of the C=O frequency towards shorter wavelength is observed. The unmodified C=O frequency of the ester does not make its appearance at all in these cases. These are denoted as (a) in Table IV and the shifts of the C=O frequencies are given in cm⁻¹ as (*a*₂₀) etc. Examples of this category are phenyl cinnamate in chloroform and coumarin in various solvents

(ii) Those in which the appearance of a modified C=O frequency (towards shorter wavelengths) is noted in addition to the original C=O frequency of the ester. These are denoted by (b) in Table IV and the frequency differences between the two are given in cm⁻¹ as (*b*₂₀) etc. Mixtures of most of the substances with phenol belong to this class.

(iii) This represents the cases where the C=O frequencies of the esters are found to become diffuse towards the shorter wavelengths. Cases of ethyl acetate in alcohol, phenyl benzoate in chloroform etc. belong to this group and they are represented as (c)

(iv) This group embodies the cases where no change has been observed in the C=O frequency of the carbonyl compound. These are denoted as (d).

Among the examples of this type may be mentioned the mixtures of ethyl benzoate and chloroform, ethyl benzoate and ethyl alcohol, etc

The following table gives a consolidated statement of the changes undergone by the C = O frequencies

TABLE IV

Name of the compound	C=O frequency of the pure substance	In chloroform	In methyl alcohol	In ethyl alcohol	In phenol
Ethyl acetate	1739	<i>d</i>	<i>c</i>	<i>c</i>	
Ethyl benzoate	1720	<i>d</i>	<i>d</i>	<i>d</i>	<i>b</i> ₂₅
Ethyl cinnamate	1712	<i>c</i>	<i>d</i>	<i>d</i>	<i>b</i> ₂₇
Phenyl acetate	1766	<i>b</i> ₂₀	<i>b</i> ₂₀	<i>b</i> ₂₀	<i>b</i> ₅₀
Phenyl propionate	1760				<i>b</i> ₅₀
Phenyl benzoate	1740	<i>c</i>			<i>b</i> ₂₈
Phenyl cinnamate	1742	<i>a</i> ₁₈	<i>c</i>	<i>c</i>	
Benzyl acetate	1745	<i>d</i>			<i>b</i> ₂₈
Coumarin	1742	<i>a</i> ₂₂	<i>a</i> ₂₂	<i>a</i> ₂₂	<i>a</i> ₂₂

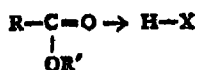
With a view to make sure that the changes observed in the C = O frequencies are not due to the effect of mere dilution, mixtures of some of the esters with the solvents benzene and carbon tetrachloride which act only as diluents were studied and Table V gives the results. The C = O frequencies are unaffected in these solvents.

TABLE V

Name of the substance	C=O frequency in pure state	C=O frequency in CCl ₄ solution	C=O frequency in benzene solution
Ethyl acetate	1739	1740	1740
Ethyl benzoate	1720	1718	1721
Ethyl cinnamate	1712	1712	1712
Phenyl acetate	1766	1763	1760
Phenyl cinnamate		1742	1740

Discussion of the Results

From the results presented in Table IV it is clear that in a large number of cases the Raman line attributable to the C = O group has been affected. The influence of the mixture is felt in one of three ways, viz, (1) a shift of the C = O line, (2) an appearance of a new line and (3) a diffuseness of the same, all taking place towards shorter wavelengths. These changes can be taken as evidences for the formation of hydrogen bonds as represented below:—



It is reasonable to assume that the extent of the lowering of the $C=O$ frequency gives an indication of the weakening of the $C=O$ link due to hydrogen bond formation and consequently it affords a measure of the strength of the hydrogen bond involved. From the large number of cases examined it is clear that these bonds vary very widely in strength depending upon the components of the mixtures.

Taking the series of mixtures with phenol it is evident that hydrogen bonds are formed very markedly. The strongest bonds are noticed with esters having the highest $C=O$ frequencies. It is consequently definite that the higher the anionoid power of the $C=O$, *i.e.*, the greater its capacity to act as donor, the stronger is the hydrogen bond formed. Methyl and ethyl alcohols behave very similar to one another. Though as a rule the hydrogen bonds formed with these solvents are weaker than in the case of phenol, similar gradation in the strengths of the bonds with the change in the $C=O$ frequencies are noticeable. In the case of chloroform the number of examples of hydrogen bond formation are fewer and the bonds are weaker. It is only with esters of very high $C=O$ frequencies that any effect is noticed.

These differences in the capacities of the different solvents to form hydrogen bonds is obviously due to the differences in the cationoid power of the hydrogen atoms involved. Phenol is, of course, the best and this is to be attributed to the presence of a phenyl ring producing a positive field by withdrawing electrons as represented below.



This explains also why it behaves as a weak acid. Alcohols are comparatively weaker due to the lack of such an electron sink. However, owing to the capacity of the oxygen atom to take a negative charge the hydrogen atom attached to it is sufficiently cationoid to form hydrogen bonds. The weakness of chloroform is to be attributed to the linking of hydrogen with carbon, an atom which shows very little tendency to take a charge. In spite of the existence of three chlorine atoms which produce positive inductive effect, the cationoid power of the hydrogen is small compared with some of the hydroxylic compounds. This agrees with the general behaviour of carbon compounds wherein even the reactive methylene groups exhibit very little tendency to produce hydrogen ions. Thus the general expectation that the strengths of hydrogen bonds depend upon (1) the anionoid power of the donor and (2) the cationoid power of the acceptor is amply substantiated.

Further cases of hydrogen bond formation leading to a full discussion of the results will be described in the subsequent communications.

Summary

A brief survey of the existing literature on hydrogen bonds is made. The advantages of employing the Raman effect for investigations in this field are discussed. The results not only supplement those obtained from infra-red studies but they become more definite, particularly when such groups as the $C=O$, which yield sharp Raman lines, are employed.

Hydrogen bond formation between various esters as donor molecules and phenol, alcohols and chloroform as acceptor molecules has been studied and the results are presented in this paper. The changes in the $C-O$ frequencies are classified. It is shown that there are large variations in the strengths of hydrogen bonds. The generalization that the strengths of hydrogen bonds depend on the anionoid power of the donor and the cationoid power of the acceptor atoms is made as a logical consequence of the mechanism of hydrogen bonds and is supported by the experimental results that are recorded.

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STUDIES IN THE FRIEDEL-CRAFTS REACTION

Part VII. The Action of Phthalic and Succinic Anhydrides on Resorcinol Derivatives

BY R. D. DESAI AND F. FIGUEROA

(From the Department of Chemistry, St. Xavier's College, Bombay)

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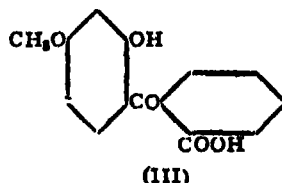
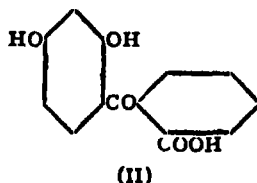
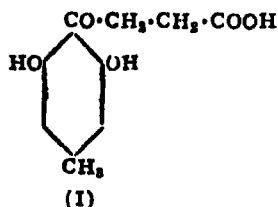
AROMATIC hydrocarbons, and phenolic ethers have been condensed with succinic anhydride in the presence of anhydrous aluminium chloride with the formation β -benzoyl-propionic acid derivatives. Ullmann and his co-workers¹ have condensed phthalic anhydride with phenol and its homologues, while Mitter and De² and Raval, Bokil and Nargund³ have condensed the same phenols with succinic anhydride. So far, these anhydrides have not been condensed with di-hydric and tri-hydric phenols, and Dalal and Nargund⁴ have reported their failure to condense resorcinol with succinic anhydride.

Desai and (Mrs.) V. H. Shroff⁵ have shown that it is possible to condense resorcinol and orcinol with succinic anhydride, though the yield of β -2,4-dihydroxy-4-methylbenzoyl-propionic acid (I) from orcinol was not satisfactory. Moreover, the reaction between orcinol and succinic anhydride gave another instance of γ -substitution which is rare.

We have now condensed phthalic anhydride with resorcinol itself, as well as its mono and dimethyl ethers, resacetophenone, β -methyl resorcyate, hydroquinone, and pyrogallol, in the presence of anhydrous aluminium chloride. Resorcinol gave a good yield of *o*-2,4-dihydroxybenzoyl-benzoic acid (II) which, on Clemmenson reduction gave *o*-2,4-dihydroxybenzyl-benzoic acid. Resorcinol monomethyl as well as dimethyl ether gave the same acid, and as it gave positive ferric chloride reaction, it must be *o*-2-hydroxy-4-methoxybenzoyl-benzoic acid (III). Mitter and De⁶ have also observed the demethylation of one of the methoxyl groups in the condensation of resorcinol dimethyl ether with succinic anhydride. Resacetophenone, β -methyl resorcyate, hydroquinone, and pyrogallol did not condense with phthalic anhydride.

Finally the bromination as well as the Clemmenson Reduction of β -2,4-dihydroxybenzoyl-propionic acid to γ -2,4-dihydroxyphenyl-butyric acid was

studied as we required this acid for some other synthetic purpose. The mono- and dimethyl derivatives of the bromo-keto-acid have been prepared, and their constitutions have been determined, as the same acids are obtained by brominating the keto-acids obtained from succinic anhydride and resorcinol mono- and dimethyl-ethers by Dalal and Nargund ⁷



Experimental

O-2 4-Dihydroxybenzoyl-benzoic Acid—To a solution of resorcinol (11 g) and anhydrous aluminium chloride (27 g) in nitrobenzene (150 c c), phthalic anhydride (15 g) was slowly added, and the mixture was heated on water-bath for 6 hours after keeping at the ordinary temperature for 48 hours. Having decomposed the aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was distilled off in steam. The solid that separated out on the addition of sodium chloride to the solution was filtered off. The crude acid, after purification through dissolution in the sodium carbonate solution, crystallised from dilute alcohol in pale-yellow needles, m p 202° (yield = 5 gm). Its alcoholic solution gave wine-red coloration with ferric chloride. [Found C, 64.7; H, 4.2, $\text{C}_{14}\text{H}_{10}\text{O}_6$ requires C, 65.1; H, 3.9 per cent.]

The *mono-bromo* derivative obtained by adding bromine (0.3 c c) in glacial acetic acid (2 c c) solution to the acetic acid solution (20 c c) of the acid (10.5 g) crystallised from benzene in plates m p 220° [Found. Br, 23.4; $\text{C}_6\text{H}_8\text{O}_6\text{Br}$ requires Br, 23.7 per cent.]

Reduction to O-2 4-dihydroxybenzyl-benzoic Acid—A mixture of the keto-acid (2 g), amalgamated zinc (10 g) and dilute (1:1) hydrochloric acid (50 c c) was heated on sand-bath under reflux for six hours. The cooled solution was extracted with ether, the solution dried, and the acid recovered. It crystallised from benzene in tiny needles, m p 143° [Found C, 68.5; H, 5.2, $\text{C}_{14}\text{H}_{12}\text{O}_4$ requires C, 68.9; H, 5.0 per cent.]

Condensation of Resorcinol Monomethyl Ether with Phthalic Anhydride and Formation of O-2-hydroxy-4-methoxy-benzoyl-benzoic Acid—To a solution of resorcinol monomethyl ether (6.2 g) and anhydrous aluminium chloride (13.5 g) in nitrobenzene (7.5 c.c.) phthalic anhydride (7.5 g) was

slowly added with constant shaking. After keeping at the room temperature for 48 hours, the mixture was heated on the water-bath for two hours. Having decomposed the excess of aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was steam distilled off, and the solid that separated on cooling was filtered off. After purification through sodium bicarbonate solution, the acid crystallised from dilute alcohol in needles, m.p. 165° . Its alcoholic solution gave wine-red coloration with ferric chloride. [Found. C, 65.8, H, 4.5, $C_{15}H_{12}O_6$ requires C, 66.2, H, 4.4 per cent.]

The *mono-bromo* derivative crystallised from alcohol in needles, m.p. 203° . [Found Br, 22.6, $C_{15}H_{11}O_6Br$ requires Br, 22.8 per cent.]

Condensation of Resorcinol Dimethyl Ether with Phthalic Anhydride and Formation of O-2-hydroxy-4-methoxybenzoyl benzoic Acid—A solution of resorcinol dimethyl ether (7 g.) phthalic anhydride (7.5 g.), anhydrous aluminium chloride (13.5 g.) in nitro-benzene (75 c.c.) was heated on the water-bath for two hours after keeping at the room temperature for 24 hours. The product worked up in the usual manner crystallised from dilute alcohol in needles, m.p. 165° , undepressed by the acid prepared from presorcinol monomethyl ether (Yield = 3 gm.)

Clemmenson Reduction of β -2:4-dihydroxybenzoyl Propionic Acid to γ -2:4-Dihydroxyphenyl-Butyric Acid—The keto-acid was prepared by the method of Desai and (Mrs.) V. H. Shroff (*loc. cit.*). Its *mono-bromo-derivative* crystallised from alcohol in needles, m.p. 190° . [Found Br, 27.5; $C_{10}H_9O_5Br$ requires Br, 27.7 per cent.]

On methylation with dimethyl sulphate in presence of 10 per cent caustic soda, the *mono-bromo acid* gave *O-5-bromo-methoxy-2-hydroxybenzoyl-propionic acid*, which crystallised from alcohol in needles, m.p. 203° . [Found. Br, 26.1; $C_{11}H_{11}O_5Br$ requires Br, 26.4 per cent.]

The same *bromo-acid* was also obtained by the bromination of *O-4-methoxy-2-hydroxy-benzoyl-propionic acid* which was prepared by the condensation of resorcinol monomethyl ether with succinic anhydride. When this acid was further methylated with dimethyl sulphate in presence of anhydrous potassium carbonate in acetone solution, the acid, m.p. 179° , and crystallising from dilute alcohol in needles was obtained. Its alcoholic solution did not give any coloration with ferric chloride. [Found Br, 24.8; Calc. for $C_{12}H_{12}O_5Br$ Br, 25.2 per cent.]

This acid proved to be *O-5-bromo-2:4-dimethoxybenoyl propionic acid* as it was also obtained by the bromination of the known *O-2:4-dimethoxybenzoyl-propionic acid* of Dalal and Nargund. The *Clemmenson reduction*

was carried out as usual and the γ -2, 4-dihydroxyphenyl butyric acid crystallised from benzene in small plates, m p 105° [Found: C, 61.0; H, 6.2; $C_{10}H_{12}O_4$ requires C, 61.2, H, 6.1 per cent]

We take this opportunity of thanking the Principal Rev. Father A. M. Coyne, S.J., and (late) Prof. R. N. Bhagwat, for their kind interest in this work

Summary

Phthalic anhydride has been condensed with resorcinol with the formation of *O*-2, 4-dihydroxybenzoyl benzoic acid. [Some derivatives of this keto acid have been described.]

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A STUDY OF THE CONSTITUENTS OF THE SEEDS OF *CROTON SPARSIFLORUS* (MORUNG)— PART I

BY S. V. ANANTAKRISHNAN, S. ARAVAMUTHACHARI
AND

V. S. GOVINDARAJAN

(From the Chemical Laboratories, Annamalai University, Annamalai Nagar)

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A—Preliminary Examination of the Seeds

ONLY two species of the genus *Croton* (family, Euphorbiaceæ), *Croton tiglium* and *Croton elliotianus* [*Meglocarpus* (Hutch)] appear to have been studied in any detail, the former being more thoroughly investigated on account of the physiological activity of the oil. The third member of the genus forms the subject of the present study. The study of this genus is highly interesting since the oils obtained from the seeds of the different species of this genus, vary considerably from one another in their properties.

Apart from a preliminary note by one of us,² there appears to have been no chemical investigation of the seed fat of *Croton sparsiflorus*. This plant (*Eliamanakku* and *Naimilakkai* in Tamil and *Kukka Mirapa* in Telugu) is a wild weed, almost becoming a menace to agriculturists and gardeners in South India. It appears to have spread from Bengal where the plant has been imported from South America about the year 1895. Mayuranathan¹¹ gives a detailed description of the plant. The leaves, the latex and the oil to some extent seem to be used locally as a dermatocide. The whole plant has been reported¹ to contain sufficient potash and nitrogen to be useful when composted as green manure.

The seeds are small and shiny and resemble castor beans. The ripening and the dispersal of the seeds normally take about 10–15 days. The seeds are so small that in the investigation the kernels are not separated, the whole seed being crushed before extraction. On an average a hundred seeds sun-dried for a week, weigh about 0.73 g. and analyse as in Table I.

On extraction successively with several solvents in a Soxhlet, the different amounts were as in Table II.

TABLE I

Analysis of the Whole Sun-dried Seeds

	%	Solvent	% on sun-dried seeds
Moisture	8.03	Petroleum ether (50–60° C)	32.67
Solvent extractables	38.44	Ether	1.37
Cake (by difference)	53.53	Chloroform	1.19
		Ethylacetate	2.19
		Alcohol	1.02

TABLE II

The petroleum ether extract gave a clear yellow oil, practically tasteless with a not disagreeable odour (the carbon tetrachloride extract in the earlier work seems to have given a different result). The oil visibly thickens on exposure to atmosphere and a drying time of 120 hours compares favourably with about 95 hours for raw linseed oil (Calcutta) and suggests its use as a drying oil.

The ether extract resulted in what appears to be three constituents, a white crystalline solid, a colourless amorphous body with a fibrous look and a brown oily liquid. The extract has a strong 'amylic' odour and was irritating to the mucous membrane.

The chloroform extract gave besides the amorphous substance obtained with ether, a darker brown oil somewhat greenish by reflected light. The irritating odour of this extract was characteristic and the substance re-dissolved in chloroform only with difficulty. Fractional precipitation with petroleum ether separated a dirty green amorphous powder, the filtrate from which left a fibrous looking product that could be recrystallised from dioxane to a high melting solid. This has not yet been further investigated.

Extraction with ethylacetate gave a waxy solid that did not re-dissolve in the solvent.

The final extraction with ethyl alcohol gave a dark viscous product which answered the common tests for alkaloids. The Prollius fluid extract also gave positive tests with alkaloidal reagents.

The neutral water extract showed evolution of carbon dioxide and frothing on warming. The extract did not answer tests for reducing substances. Steam distillation of the seeds gave no volatile products.

The analysis of the 'cake' left after the petroleum ether extraction of the oily constituents indicates a very high fibre content and a good percentage of proteins.

The ash content of the seeds was 3.62% and analysed as in Table IV. The high percentage of phosphorus, calcium, sodium and potassium in the ash and sufficiency of nitrogen in the 'cake' suggests the utility of the meal as manure.

The meal from the oil extracted sample was tested for the hydrolysis of olive oil which established the presence of a lipolytic enzyme in the 'cake'. A qualitative comparison with the castor bean meal which is known to contain a lipase in a very active form showed that the lipase present in this seed is not as active as that in the castor bean.

TABLE III
Analysis of the 'Cake'

	%
Nitrogen (Kjeldahl)	4.97
Proteins (calculated)	31.05
Fibre	37.5

TABLE IV
Analysis of the Ash of the Seeds

	%
Iron as Fe_2O_3	Trace
Calcium as CaO	21.43
Sodium as Na_2O	16.70
Potassium as K_2O	14.33
Phosphorus as P_2O_5	29.88
Silica	13.88
Carbonate (by difference)	3.78

B—The Physical and Chemical Constants of the Oil

As indicated in the previous section, the seeds contain a high proportion of fixed oil most of which can be extracted with petroleum ether. The physical and chemical constants of this oil have been determined by usual methods and are collected in Tables V, VI and VII.

TABLE V
Physical Constants of the Oil

Colour (visual)	Light yellow
Odour ..	Resembles linseed oil
Specific gravity $\cdot d_{4}^{20}$	0.9270
Refractive Index (Abbe)	1.4753
n_{D}^{20}	1.4709
$n_{D}^{40.0}$	
Viscosity (in millipoises)	28.85

TABLE VI
Chemical Constants of the Oil

Acid Value	9.18
Saponification Value	189.5
Do (in an atmosphere of nitrogen)	190.3
Saponification equivalent (calculated)	295.4
Ester Value (calculated)	180.72
% Glycerine	9.88
Acetyl Value	0.02
Iodine Value (Rosenmund-Kuhn-henn) (see also Table VII)	163.4
Thiocyanogen-Iodine Value	90.41
Mehner Value	91.96
Hexabromide Value (Steele and Washburn)	10.99
Reichert-Meissl Value	1.10
Polenske Value	4.18
Percentage unsaponifiable matter (Kerr-Sorber)	1.36
Do. (continuous extraction)	0.98
Maleic anhydride Value	3.3
Drying time of film	about 120 hours

TABLE VII
Iodine Value of the Oil by different methods

Method	Reagent	Value
Wijs	Iodine monochloride	172.0
Winkler	Sodium bromide, sodium bromate and hydrochloric acid	168.1
Hanus	Iodine monobromide	163.1
Kaufmann	Alcoholic bromine (with sodium bromide)	163.9
Rosenmund-Kuhnhenr	Pyridine sulphate-dibromide	163.4

The high iodine value comparable with that of raw linseed oil indicates a possible use of this oil as a substitute.

Hexabromide values have been usually determined by two methods but tropical temperatures preclude the adoption of the Eibner and Muggenthaler method that involves filtration of ether solutions. This method did not yield in our hands pure hexabromo-stearic acid and also gave a very high value. Lewkowitsch⁹ also considers that the results obtained by this method are unaccountably high. The method of Steele and Washburn¹⁰ has therefore been adopted for the determination of this value.

The Kerr-Sorber method modified by Jamieson and co-workers^{7a} for the determination of the unsaponifiable matter in oils involves the ether extraction of a dilute solution of the soap in a separatory funnel. The extraction of appreciable amounts of soap on account of the high laboratory temperature and the formation of stubborn emulsions render this method tedious and of doubtful value. Knapp⁸ has shown that this method does not give an accurate estimate of the unsaponifiable matter and that the use of a continuous extractor in the determination has numerous advantages besides a more correct estimation of the percentage of unsaponifiables. The extractor used in the present study, following that designed by Kutsher and Steudd, was similar to that described by Knapp with this modification that the solvent distributor had a flat glass spiral on it, thus ensuring greater circulation of the soap solution. The design of the apparatus allows the maintenance of the extractor at any desired temperature.

The somewhat lower value obtained for the unsaponifiable matter by the continuous extractor method is to be attributed to the complete absence of dissolved soap in the final unsaponifiable matter collected, which is not excluded in the alternative method.

The maleic anhydride value of 3.3 (Ellis and Jones method⁶) may be taken to show the presence of some conjugation. However, it is difficult

to take this as conclusive evidence of any conjugation since it has been shown^{4,5} that neither this nor the method of Kaufmann indicate accurately the extent of conjugation in oils of low diene numbers

The drying time for a thin film of the oil is sufficient indication of the 'drying' properties of the oil. The drying time of 120 hours seems satisfactory for the purpose of a drying oil.

A deep blue colour with arsenophospho-tungstic acid is considered to indicate the presence of linolenic acid in the glyceride in the absence of acids of higher unsaturation¹⁰. The oil under investigation gave a positive test, though the intensity (visual) is much less than with raw linseed oil.

Experimental

Fully ripe seeds sun-dried for a week were used, and were taken to represent the initial sample in the analysis of seed constituents.

The moisture content was determined by the usual method of drying in an oven at 110° C.

Since the oil polymerises readily, only the sun-dried seeds were used for the determination of solvent extractables, the extraction being carried out in a Soxhlet.

The 'cake' was analysed for the protein, fibre and enzyme content. Nitrogen was estimated by Kjeldahl's method using 0.05 g selenium as catalyst and 0.5–1.0 g of cake.

The fibre content was estimated by usual methods³. The presence of a lipolytic enzyme was established by the method of Willstätter¹⁵.

The seeds were ashed at a dull red heat and the several components determined by standard methods of quantitative analysis.

For the determination of the physical and chemical constants of the oil, a petroleum ether extract of the seeds freed from solvent was used. Crushed sun-dried seeds were packed in an extractor of a modified form of Wester's apparatus¹⁴ and the oil extracted with petroleum ether (50–60°). The extract was filtered off from any plant material that might have been mechanically carried through, dried over anhydrous sodium sulphate, and the major portion of the solvent was distilled off. The last traces of solvent were removed under reduced pressure (1–2 mm). The oil was stored in a brown bottle in an atmosphere of carbon dioxide.

Refractive indices were determined at 29.5° and at 40° using an Abbe refractometer.

Viscosity measurements were made with an Ostwald viscometer, 'conductivity' water and anhydrous, thiophene free, crystallisable benzene of the correct melting point were used for comparison. The measurements were carried out at 30.2°. Taking the viscosity of water as standard from Landolt's tables and using the relation

$$\frac{\eta_1}{\eta_2} = \frac{S_1 t_1}{S_2 t_2}$$

the viscosity of the oil in millipoises was calculated

Other constants were determined by standard methods.⁷ In the determination of the saponification value thymolphthalein was found to be the best indicator both for macro- and semi-micro-determinations of the value

In the determination of the thiocyanogen-iodine value the reagent was prepared by the method of Gardner and Weinberger. The acetic acid used was the Hopkin and Williams product, purified by the method of Orton and Bradfield.¹² This acid mixed with 10% acetic anhydride ANALAR was used as the solvent. The reagent was stored in a dry amber coloured bottle and tightly stoppered. The reagent was prepared fresh for each estimation. Polymerisation was noticeable on storage.

The method of Knapp⁸ was followed in all details in the determination of the unsaponifiable percentage using a continuous extractor. Aliquots from the saponified solution, made up to a definite volume, gave closely comparable values.

The drying test was carried out by usual methods. Raw linseed oil (Calcutta) dried in 95 hours while the oil under investigation dried in 120 hours to the same consistency.

The oil gave a positive test for vitamin A with antimony trichloride.

Summary

The constituents of the seeds of *Croton sparsiflorus* have been examined and the physical and chemical constants of the petroleum ether extractable fixed oil have been determined.

The authors thank the Superintendent, Government Test House, Alipore, for an analysed sample of raw linseed oil that was used for comparison and standardisation of experimental conditions.

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A STUDY OF THE CONSTITUENTS OF THE SEEDS OF *CROTON SPARSIFLORUS* (MORUNG)—PART II

Chemical Examination of the Components

BY S V ANANTAKRISHNAN, S ARAVAMUTHACHARI

AND

V S GOVINDARAJAN

(From the Chemical Laboratories, Annamalai University, Annamalainagar)

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It has been noticed in Part I that the petroleum ether extract contains most of the solvent extractables and this extract has been used for a more thorough investigation as to the component "resins", unsaponifiables and glycerides

While the formation of a deep red colour on refluxing with alkali may be indicative of the presence of a resinous component, neither the method of Flaschentrager and Wollfersdorff⁶ who isolated the poisonous resinous component or 'Naturstoff' from *Croton tiglium*, nor the more general methods described in text-books gave any appreciable quantity of such a substance in a sufficiently pure state for a complete study. That any such component is present at best in minute amounts only is indicated from the physical and chemical constants of the treated oil which shows no appreciable difference. The method of Cherbuliz² also gave a similar result.

The colour with alkali is presumably due to the colouring matter in the seed coat

As may be expected, the oil contains unsaponifiable matter which could be separated into several components which are still under investigation. A sterol, m.p. 138°, (α) $\frac{29.8^\circ\text{C}}{8400^\circ}$ ($C=0.8013$) = 56.27 has been isolated. Microscopic examination of the sterol, melting point of the sterol and of the acetyl derivative and the rotation indicate this to be a phytosterol largely consisting of α -sitosterol.

Component Acids—The chemical examination of the fat may be considered under two heads, the nature of the glycerides and the component acids in the glyceride. Information regarding the latter can be obtained in several ways, and the components definitely established are given in Table I

TABLE I

Distribution of component acids in the oil (by weight %)

Component acids	Total % in oil	Component acids	Total % in oil
Palmitic	5.49	Linolenic	9.36
Stearic	4.75	Unsaponifiable matter	0.98
Oleic	5.72	Glycerine (by difference)	8.02
Δ ⁹ 12-octa-decadienoic	65.70		

The Hehner value indicates 91.96% of acids saturated and unsaturated together with unsaponifiable matter in the oil. These components were obtained after saponification under standardised conditions (*vide* experimental part). The separation of solid and liquid components has been effected by Twitchell's lead salt alcohol method,³⁰ some modification, of the same¹⁰ and by direct crystallization from acetone solution.²⁵ The results of these different methods are appended in Table III.

Mention should be made here of the relative accuracy of the different methods. Repeated trials have shown that Bertram's oxidation method gives accurate results for saturated acids provided the conditions of temperature are maintained so as to completely eliminate hydroxy acids arising from the unsaturated acids (see also Gay⁷ and Hilditch and Priestman¹²).

The modified lead salt-alcohol method¹⁰ has been consistently found to yield more accurate results and a purer solid acid than other methods involving lead salts. Rigid control of temperature at 15–16° C for twelve hours is absolutely necessary for concordant results.

As the methods of separation do not completely eliminate liquid acids, a correction factor based on the iodine value of the two fractions¹⁶ has to be used for an accurate estimation of solid acids.

With reactive unsaturated compounds and with possibilities of isomerization catalysed by the saponifying reagents, lead salt methods are liable to lead to some uncertainty arising from the greater or different solubilities of some of the lead salts. Physical methods of separation are preferable and in the present case, crystallization of the acids in acetone solution at different temperatures have been adopted.

It will be noticed that the component acids are mostly liquid (90%) and these have a high iodine value (Tables II and III).

TABLE II

Method	Refer- ence	Weight % in acids			Liquid acids (by dif- ference)	Weight % in oil*	
		Solid acids				Solid acids	Liquid acids
		Found %	Iodine value	Corrected %			
Twitchell lead salt alcohol	(30)	10.92	15.54	9.92	90.08	9.03	81.95
Modified Twitchell lead salt alcohol	(10)	10.85	6.30	10.45	89.55	9.51	81.47
Ba gman-Jamieson lead salt ether	(16)	16.78§	30.20	13.80	86.20	12.55	78.43
Bertram oxidation (modified)	(16)	11.25‡		11.25	88.75	10.24	80.74
Crystallization method	(25)	10.90				9.92	81.06

* Calculated for 90.98% of total acids (Hegner value—unsaponifiable %) in oil from corrected values

§ Calculated from the value 15.27, obtained for per cent of saturated acid, direct from oil.

‡ Calculated from the value 10.24 for per cent of saturated acid, direct from fat

TABLE III

Details of analysis	Total acid	'Solid' acid	'Liquid' acid (by difference)
Weight % on total acids	100	11.25	88.75
Iodine value (Rosenmund-Kuhnemann)	165.7	0.1	169.5
Thiocyanogen value	91.34		92.12
Mean molecular weight	289.3	265.5	1233*

* The high molecular weight of the liquid acids may be due to polymerisation by inter-molecular addition of the unsaturated acids

The solid acids obtained are essentially palmitic and stearic acids. Partial separation of the acids was effected by fractional distillation of the methyl esters under reduced pressure, the rich fractions being used for the preparation and identification of the pure acids. The final estimate of the relative proportions were made by the method of thermal analysis and molecular weight determination

In establishing the relative amounts of the different unsaturated acids present, bromination, partial oxidation, fractional distillation of methyl esters and Kaufmann's method using thiocyanogen-iodine and iodine values have been employed

The formation of an ether insoluble crystalline hexabromostearic acid (m p. 182°C) while indicative of the presence of linolenic acid in the oil cannot always be taken to be quantitatively representative of the triolefinic acid content (Rollet,²³ Erdman and Bedford⁶ and McCutcheon²²) The low hexabromide value combined with the high iodine value indicates a high proportion of linoleic acid with smaller amounts of oleic and linolenic acids However, bromination of the mixed fatty acids failed to yield any solid tetrabromide characteristic of α -linoleic acid usually found in seed fats The high bromine content (50.29%) of the oily liquid from the separation of the hexabromide indicates the presence of a peculiar C_{18} -diethenoid acid This is considered in greater detail in a later section

Controlled oxidation of the acids may also be expected to give an insight into the component acids The method of Lapworth and Mottram²⁰ was found unsatisfactory and that of Hilditch and Jasperson²¹ has been adopted An impure product, m p $124\text{--}126^{\circ}$, from which only a very small amount of tetrahydroxy-stearic acid (m p 172°C) could be isolated was obtained After recrystallization only impure dihydroxy-stearic acid could be obtained This was obtained in a pure state and in sufficient amounts by a slight modification of the process (Experimental) The isolation of this product connotes the presence of oleic acid in the glyceride No keto-stearic acid was isolable in the process and only small amounts of hexahydroxy acid could be got

Complete oxidation of the methyl esters of 'liquid' acids in acetone with potassium permanganate (weakly alkaline) gave *n*-hexoic, oxalic and azelaic acids The formation of these indicate the presence in the original mixture of $\Delta^{8,12}$ -linoleic and linolenic acids

The close boiling points of the methyl esters ruled out the separation of the constituent acids by fractional distillation of the esters under reduced pressure and all attempts failed to separate the constituents.

It has been found¹⁸ since Kaufmann's thiocyanogen-iodine number determination that a combination of this with iodine values can be used for computing the proportions of the unsaturated acids If a mixture contains S% saturated acids, X% linolenic, Y% linoleic and Z% oleic acids then

$$100 \times (\text{iodine value}) = 273.7X + 181.1Y + 89.9Z$$

$$100 \times (\text{thiocyanogen value}) = 182.5X + 90.5Y + 89.9Z$$

$$100 = X + Y + Z + S$$

If S is determined by any of the usual methods, X, Y and Z can be calculated. The results of such a computation are given below:

TABLE IV
Distribution of Fatty Acids in Mixed Acids

Acids	Kaufmann method (weight %)	Bromination method (weight %)
Saturated (Bertram)	11 14	11 14
Oleic	6 30	*
Δ^8 18-octa-decadienoic	72 28	*
Linolenic	10 28	4 04

* The iodine value of the remaining unsaturated acids after allowing for the observed amounts (4 04) of linolenic acid, corresponding to the hexabromostearic acid isolated, was still in excess of that of linoleic acid. This is, in itself, proof that linolenic acid is not completely separated as insoluble hexabromide. It will also be noted that the bromination method records only 39.25% of the linolenic acid content indicated by thiocyanometric analysis.

Though the accuracy of this method has been questioned,³¹ it now appears from the work of Hilditch and co-workers^{13, 14} that the method is fairly accurate (see however Smith and Chibnall²⁶).

C₁₈ Acids—It is necessary, at this stage, to consider in greater detail the C₁₈ acids, especially the unsaturated acids.

The formation of hexabromostearic acid (m.p. 182°) by bromination and of dihydroxy stearic acid (m.p. 131°) by controlled oxidation clearly indicate the presence of linolenic and oleic acids in the oil. The evidence for an octa-decadienoic acid is however, not so direct. According to Hilditch¹³ (see also foot-note to Table IV) the hexabromide value of an oil measures approximately 40% of the actual linolenic acid present and on this basis, the hexabromide value (10.99) corresponds to 10.1% linolenic acid in the mixture of acids from the oil. If the rest of the mixture were to contain only oleic acid (78.76) and saturated (11.14% observed value) acids, the iodine value of the total acids should be 99.26 while the actual value obtained is 165.7. This clearly indicates a higher unsaturation, than one double bond (if remaining unsaturated acid is diolefinic iodine value should be 170.3). The absence of a benzene insoluble bromide (*vide* Experimental) precludes the presence of higher unsaturation than a triethenoid type. One must necessarily conclude that a diethenoid compound is present in appreciable amounts to account for the high iodine value. Further, complete oxidation of the methyl esters leads to *n*-hexoic acid, oxalic acid (presumably from malonic acid) and azelaic acid, clearly pointing to the presence of Δ^8 18-octa-decadienoic acid (*vide* Haworth⁹).

The presence of mono-, di- and tri-ethenoid C₁₈ acids having been established, it is clear that the thiocyanometric method is the best for

estimating the relative proportions. This gives the values tabulated earlier (Table V). It is significant that with such a high percentage of $\Delta^9,12$ -octadecadienoic acid, bromination of the unsaturated acid fails to give the petroleum ether insoluble, crystalline tetrabromide (m.p. 114°) characteristic of the common or α linoleic acid but yields an oily liquid bromide soluble in petroleum ether (Bromine content 50.28%). Prolonged keeping of the oily bromide gives a small amount of a low melting waxy solid. It must be mentioned that Kass and Burr¹⁷ have obtained a similar waxy solid (m.p. 75.5–78°) from the products of bromination of elaidinised α linoleic acid. The linoleic acid present in the oil under investigation must therefore be an isomeric form. Our observations, however, are enough to show that this is not likely to be either the *cis-cis* or the *trans-trans* forms.

Evidence for conjugated unsaturation is inadequate but the small but definite maleic anhydride value and effect of weight of sample on the iodine value by Wijs and Hanus methods suggest some conjugation.

The configuration of the linoleic acid is under investigation.

Glyceride structure—The oil does not contain any fully saturated glyceride, the small quantity of solid resulting from acetone permanganate oxidation being only the unsaponifiable matter.

A preliminary study of the mixed unsaturated saturated glycerides has been made by the fractional crystallization of the brominated glycerides and comparing them with those prepared from linseed oil. The glycerides from linseed oil were separated by the method of Tom²⁹. The bromoglyceride corresponding to α -linoleo-di- α -linolenic glyceride melted even after several recrystallisations only at 153°C. Another fraction having m.p. 143° was also isolable. Following Eibner³ this has been taken to be β -linoleo-di- α -linolenic bromoglyceride.

Following Tom's procedure, the oil under study gave 17.8% of the more insoluble glyceride showing the presence of linoleo-di-linolenic glyceride in the oil. The product had a m.p. 143–144° and the m.p. was not depressed by admixture with a similar product from linseed oil. This must therefore be β -linoleo-di- α -linolenic bromoglyceride. The separation by Suzuki and Yokoyama²⁸ of two isomeric linoleo-di-linolenin from linseed oil, however, leaves this an open question and further investigation is necessary before establishing the identity of this compound. The absence of a product of m.p. 156° corresponding to the α -linoleic-di- α -linolenin indicates that α -linoleic acid is not present in the oil to any appreciable extent.

Another fraction isolated having m.p. 118° probably corresponds to triolein or oleic-linoleic-linolenic glyceride.

It is interesting to compare here the different properties of the three members of this genus.

TABLE V

Comparative Data of the Three Species of the Genus Croton

Characteristics	<i>Croton tiglium</i>	<i>Croton Elliotianus</i>	<i>Croton sparsiflorus</i>
Physiological	A powerful vesicant an irritating purgative	Non-vesicant non-irritating purgative	Non-vesicant no purgative action
Colour	Dark yellow	Yellow	Light yellow
Type of oil	Non-drying	Drying	Drying
% Yields of oil on seeds	50	30	32
Iodine value	102-108	143-147.5	164-171

TABLE V—Contd

Component Fatty Acids (Weight %)

Acids	<i>Croton tiglium</i>	<i>Croton Elliotianus</i>	<i>Croton sparsiflorus</i>
Palmitic	1.30*	10.0†	5.97
Stearic	0.50	}	5.17
Oleic	55.80		6.30
Linoleic	28.80	80.0	72.28‡
Other unsaturated acids	Traces of steam volatile lower acids		Linolenic 10.28
Observers	Fiaschentrager and Wollfiersdorff ⁶	Imperial Institute ^{2a}	Present work

* Also 11.3% myristic and 2.3% arachidic acids.

† Chiefly palmitic

‡ The acid is an isomer of usual seed fat linoleic acid

The constituent acids conform to the general observation that the Euphorbiaceæ seed fats contain about 10% saturated and about 80% unsaturated acids but *Croton tiglium* differs from the other two in the nature of the saturated acids. The oil under investigation is also exceptional in containing linolenic acid and no steam volatile components.

Experimental

Preparation of acids—The best procedure after several trials was found to be the following: 100 parts of the oil were refluxed on a steam-bath for four hours with a solution of 40 parts of potassium hydroxide in 500 parts of 95% alcohol (by weight). Most of the alcohol was removed by distillation in a current of carbon dioxide, the soaps dissolved in a large volume of water and the unsaponifiable matter removed in a continuous extractor. The

free acids were obtained from this either by acidulation and extraction or by the method of Steele and Washburn,²⁷ the operations being carried out in an inert atmosphere. Completion of saponification was tested by Geitel's⁸ test. For large quantities, the second method works better.

Separation of saturated and unsaturated acids—The separation of saturated and unsaturated acids was effected by the usual standard lead salt methods and by direct crystallization. The apparatus for this last process can be constructed from common laboratory materials, namely a wide mouthed vacuum jar, a large test-tube and a thistle funnel closed by a filter paper, the arrangement being as in Fig. 1.

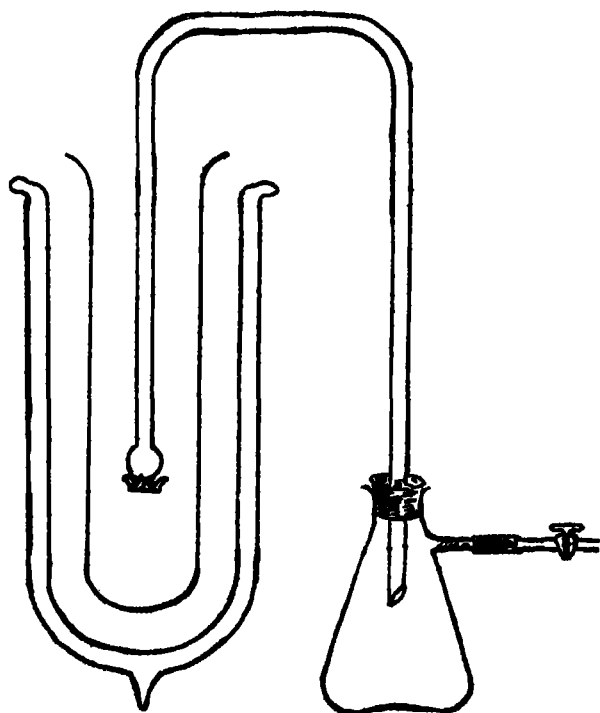


Fig. 1

A solution of the mixed acids in acetone is placed in the test-tube and cooled to different temperatures using appropriate freezing mixtures. After equilibrium at each temperature, the solution was drawn through the filter paper by suction and the residual solid washed with cooled acetone two or three times. The solids thus obtained at each stage indicated a good separation of the components. The advantage of this arrangement over that of Shinowara and co-workers²⁸ is that all filtrations and washing are carried out at specified low temperatures at which crystallization takes place.

Separation of saturated acids is complete in six hours at -19° to -22° C. From 60 gm. of the total acids 6.54 g saturated acid were obtained. The same acids were also obtained by Bertram's oxidation method modified by Jamieson¹⁸ correction for adsorbed unsaturated acids being applied by means of the iodine value. Molecular weights of the acids were determined by the usual methods.

Unsaturated acids—85.73 g of freshly separated 'liquid' acids (Twit-chell's method) were converted into the methyl esters by the usual methods and when purified 73.25 g of the mixed esters was obtained. 62.5 g of this mixture was taken in an ordinary Ladenburg flask and distilled under 1 mm pressure, using a Perkin triangle to collect the fractions. The middle bulb of the flask was two-thirds filled with glass beads supported on a thin strip of copper gauze. The three bulbs and neck were thickly coated with asbestos with slit windows for observation in order to minimise overcondensation of esters. The bottom bulb was completely immersed in an oil-bath whose temperature was maintained $50-60^{\circ}$ higher than that indicated by the thermometer at the top of the column. The results of this fractionation are given in the table below.

TABLE VI
Fractional Distillation of the Methyl Esters of the 'Liquid' Acids
(62.47 g)

No	Weight in g	Temperature at head of the column °C.	Iodine value*	No	Weight in g	Temperature at head of the column °C	Iodine value*
1	1.25	140-150§	93.6	5	7.87	158-160	154.0
2	10.95	150-154	129.4	6	14.43	160-162	169.4
3	6.84	154-156	133.7	7	12.88	Residue	
4	8.25	156-158	148.3				

* Rosenmund-Kuhnhehn method

§ A few drops collected below 140° C

All the fractions gave Martins colour test for linolenic acid.²¹

The liquid acid mixture was brominated in chloroform, ether and petroleum ether by adding excess bromine in solution and removing the excess with amylene. In each case after one or two recrystallizations pure hexabromostearic acid, m.p. $181-82^{\circ}$ C was obtained, the identity was established by comparison with an authentic specimen and by analysis. (Br found 63.6, $C_{18}H_{30}O_2Br_6$ requires Br = 63.3%.) From the residual solutions, no tetrabromostearic acid was isolable in any of the experiments. Prolonged keeping of a petroleum ether solution at or below 0° C gave rise to a low melting white solid with a bromine content of 50.29%.

Oxidation of liquid acid esters—The middle fractions from the fractionation of the methyl esters were submitted to oxidation by Haworth's method⁹ using potassium permanganate in acetone solution. After oxidation, acetone was distilled off and the residue extracted with a hot dilute solution of sodium hydroxide. The combined extracts were concentrated to 150 c.c. acidified with hydrochloric acid and ether extracted.

The presence of oxalic acid in the aqueous layer was detected by the formation of calcium oxalate, decolourization of potassium permanganate and the formation of urea oxalate. The urea oxalate was compared with an authentic specimen.

The ether extract was washed free of acid, the solvent distilled off and the residue steam distilled. The non-volatile residue was decolourised with animal charcoal in aqueous solution, filtered and allowed to crystallise. White crystals (m.p. 103°) were obtained. On recrystallization, a pure product (m.p. 105.5°, molecular weight 187.5) was got and was identified as azelaic acid.

The volatile distillate was thrice extracted with petroleum ether (50°–60°), dried over anhydrous sodium sulphate and the solvent carefully distilled off. *n*-Hexoic acid was obtained (m.p. Ca - 2°) and confirmed by the formation of an anilide (m.p. 92°) (m.p. of *n*-hexoic acid - 2°, m.p. of its anilide 95°).

Partial oxidation of liquid acids by Lapworth's method gave only dihydroxy stearic acid as a product. Dioxane was found to be the best solvent for recrystallizing this compound. (Found m.p. 131°; mol. wt. 316.2)

The method of Hilditch and Jasperson¹¹ gave better results. After oxidation with cold very dilute permanganate, the solution was decolourized with sulphur dioxide and acidified with hydrochloric acid. The precipitated crude hydroxy acid was refluxed with petroleum ether (50–60°) after drying at 65–70° C. to remove unoxidized acids. The residue after filtration was refluxed thrice with ethyl acetate (for 0.77 g. of the crude hydroxy acid, 50 c.c. of the ethyl acetate was used each time) and filtered hot. A small quantity of a white substance was left undissolved and on recrystallization from alcohol melted at 169° (one of the tetrahydroxy stearic acids melts at 172°–73° C.).

The ethyl acetate solution on cooling deposited white crystals (m.p. 124–26°) and further purification did not affect the melting point (mixed m.p. with pure dihydroxy stearic acid 128°). Equivalent weight of this compound was 241.8.

Selective oxidation.—The procedure was based on that of Kaufmann and Fiedler for oleic acid.¹⁰ Mixed acids (14.75 g.) were just made alkaline

with alcoholic potassium hydroxide, diluted to two litres with water, cooled to 0° C and oxidized with two litres of a 1% solution of potassium permanganate with efficient stirring during 30 minutes. The solution was allowed to stand for 10 minutes, acidified with sulphuric acid and decolourized with sodium bisulphite. The solid obtained was collected on the filter, the solution being examined for hexahydroxy acids.

The crude hydroxy acid (0.91 g) was taken up with a large volume of warm ether. A very small quantity (0.08 g) of a brownish substance gave on recrystallizations from alcohol a pure white product melting sharply at 172°. This is presumed to be tetrahydroxy stearic acid.

The ether extract gave a white solid which after washing with petroleum ether gave a powdery substance (m.p. 129°, equivalent weight 334.2). Recrystallization from dioxane gave pearl white flakes (m.p. 130°) confirmed as dihydroxystearic acid by comparison with an authentic specimen.

The filtrate from the original oxidized solution after separation of the crude hydroxy acid was concentrated to small bulk and acidified. The product after recrystallizations from alcohol and water was very small in quantity (m.p. 196°). Being more soluble in water than the tetrahydroxy acid and with a m.p. higher than that of the known tetrahydroxy acids, this is presumed to be hexahydroxy stearic acid. The quantity obtained was too small for definite identification.

Solid acids.—The solid acids from Twitchell's method were converted into neutral methyl esters and distilled under reduced pressure. The results of fractionation are tabulated below.

TABLE VII
Fractionation of Methyl Esters of 'Solid' Acids

Fraction No	Temperature at head of the column °C.	Weight of fraction g	Saponification value	Molecular weight	Acids identified
a	145-54	0.62	204.2	274.9	Palmitic
b	154-57	2.55	203.8	275.4	Palmitic and stearic in small amounts
c	157-60	2.61	203.5	275.7	Palmitic and stearic
d	160-62	1.63	198.2	283.1	Stearic and palmitic
e	162-64	2.23	192.1	292.1	Stearic and palmitic in small amounts
f	163-64	2.14	192.2	292.0	Do.
g	Residue including losses	0.96	192.0	292.2	.

TABLE VIII
Calculated Distribution of 'Solid' Acids

Fraction No	Palmitic acid (weight in g) calculated from ester	Stearic acid (weight in g) calculated from ester	Total acid (weight in g)
a	0.49	0.10	0.59
b	2.00	0.44	2.44
c	2.00	0.48	2.48
d	0.84	0.70	1.54
e	0.47	1.60	2.07
f	0.47	1.57	2.04
g	0.20	0.71	0.91
Total (weight in g)	6.47	5.60	12.07
% (weight) on solid acids	53.58	46.42	100
Calculated on 11.25% of mixed acids	% (weight) 6.03	5.22	11.25
	% (mole) 6.34	4.91	11.25

Pure palmitic and stearic acids were obtained from the fractions

Unsaponifiable matter.—The crude unsaponifiable matter was again saponified for one hour. The white flakes that separated out on cooling were filtered off and washed with methanol. The product answered the usual colour reactions for sterols. The Rosenheim reaction was negative indicating the absence of conjugation. The sterol was purified by precipitating as the digitonide and decomposing it with pyridine (Schonheimer and Dam²⁴). The specific rotation of the sterol was observed in chloroform solution.

TABLE IX
The Constants of the Sterol

Melting point	138° C.
Melting point of acetyl derivative	125° C.
Melting point of digitonide	Softens 206° C., melts to brown liquid 235° C.
(α) _D ²⁰ 5 (C = 0.8013)	—56.27
(α) _D ²⁰ 5 (C = 0.8013)	—32.64

Small quantities of an alcohol and a low melting solid hydrocarbon were isolated from the filtrate from sterol digitonides but the quantities were inadequate for complete investigations.

Glyceride structure.—Fully saturated glycerides were determined by the oxidation method of Hilditch and Lea¹⁵

Reference substances for Tom's method²⁹ were prepared from pure linseed oil

The oil under investigation (1 g) was brominated in ethyl acetate (10 c.c.) at about 0° C by slow addition of 1 c.c. bromine with efficient stirring. The crude bromoglyceride was separated by filtration, washed with 20 c.c. portions of ethyl acetate and dried at 80°. Further purification with alcohol, ether and tetralin gave a white substance (m.p. 143°) identical with β -linoleo-d- α -linolenin obtained from linseed oil. From the ethyl acetate filtrate a second product unidentified (m.p. 117° C) was obtained.

The authors thank the Superintendent, Government Test House, for a sample of tested raw linseed oil which was used for comparison.

Summary

The oil from the seeds of *Croton sparsiflorus* has been examined for its composition. Apart from palmitic, stearic, oleic and linolenic acids, the glyceride contains an unusual isomeric form of the common α -linoleic acid. Complete analysis of the oil has been effected by using Bertram's oxidation method and Kaufmann's thiocyanometric method. Fully saturated glycerides are absent and the oil contains β -linoleo-d- α -linolenin.

The sterol in the unsaponifiable matter is essentially sitosterol.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

Part V. Synthesis of 2-N¹-Sulphanilamido-5-alkyl- and 2-N¹-Sulphanilamido-4-methyl-5-alkyl-thiazoles

BY K GANAPATHI, M V SHIRSAT AND C V DELIWALA

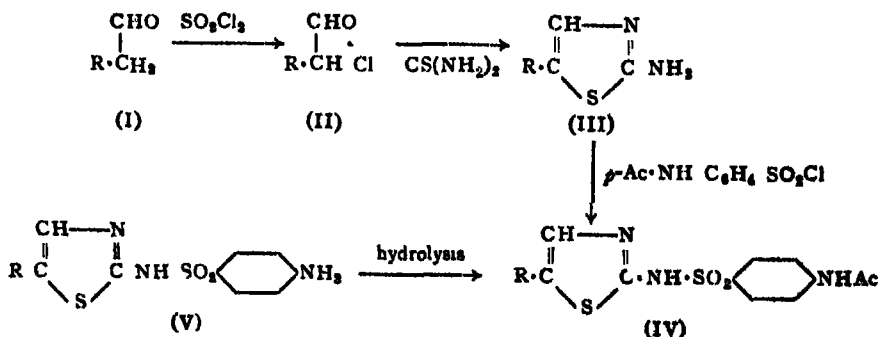
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THE studies carried out in this Institute on the therapeutic properties of a pilot series of N¹-sulphanilamido derivatives of various ring compounds in experimental *β*-hemolytic streptococcal, (type I) pneumococcal and *P. pestis* infections in mice, have led to the discovery of the outstanding therapeutic properties of 2-N¹-sulphanilamido derivatives of thiazole and pyrimidine. The clinical studies carried out hitherto, extensively with the former and to a limited extent with the latter drug, have fully confirmed the results of the animal experiments. As a sequel to this, we undertook to investigate whether, by the proper manipulation of the molecular structure of these drugs, other derivatives could not be discovered which may be more effective or therapeutically active in the treatment of those infections in which they are of little value. The synthesis of many possible types of such compounds was therefore undertaken to study systematically the effects (pharmacological and physico-chemical) of different types of additional substituents in the sulphanilamido derivatives of thiazole and pyrimidine. This paper is concerned with the synthesis of a particular series of 2-N¹-sulphanilamidothiazole derivatives with alkyl substituents in the positions 4 and/or 5 of thiazole, the other types of thiazole and pyrimidine compounds are being reported in the succeeding parts.

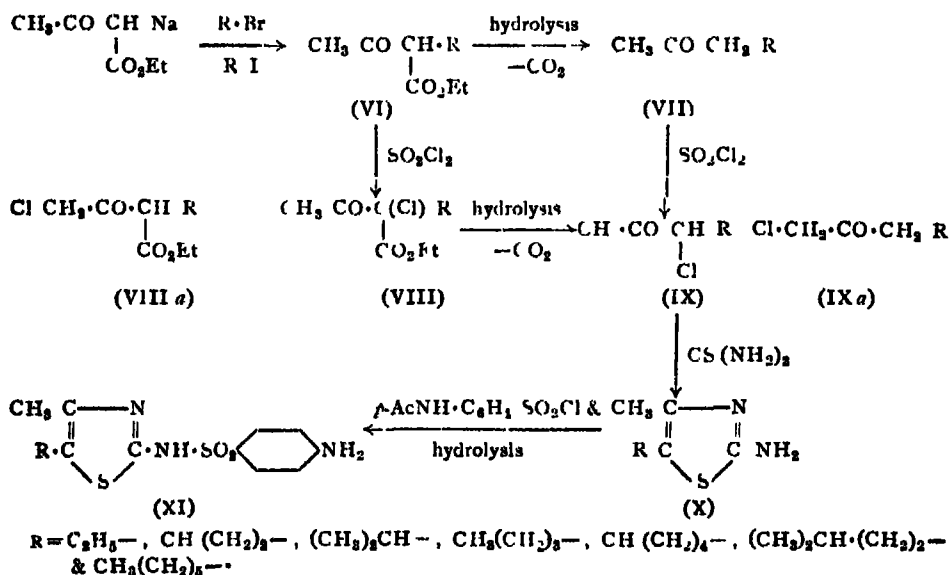
2-N¹-sulphanilamido-5-alkylthiazoles were synthesised according to the following scheme.



R = C₂H₅, Me₂CH-, CH₂(CH₂)₃- & CH₃·(CH₂)₄-

The literature regarding the halogenation of the aliphatic aldehydes (I) is very scanty. Of the 2-amino-5-alkylthiazoles (III), only the 5-methyl derivative has previously been described¹. It has now been found that the 2-amino-5-alkylthiazoles (III) can smoothly be prepared by chlorinating the alkyl aldehydes (I) with sulphurylchloride and condensing the resulting chloroaldehydes (II) with thiourea. The bromination of the aldehydes was also tried but it appeared to be less advantageous for our purpose since tarry products were formed on condensing the bromoaldehydes with thiourea. The conversion of the aminothiazoles (III) into 2-N¹-sulphanilamido-5-alkylthiazoles (V) by the usual method was effected in good yields.

The general method adopted to synthesise 2-N¹-sulphanilamido-4-methyl-5-alkylthiazoles was as follows —



In the above scheme, excepting the ketonic esters (VI), ketones (VII) and 3-chloro-2-pentanone, all other compounds are not described in the literature. The preparation of the chloroketones (IX) *via* the chloroesters (VIII) furnished purer products (though in poorer yields) evidently because, the chlorination of the ketonic esters (VI) with sulphurylchloride, as is described,^{2, 3} leads exclusively to the chloroketonic esters of formula (VIII), uncontaminated with the isomeric esters of formula (VIII a). In the chlorination of the ketones (VII) also with sulphurylchloride, it has been suggested² that the chlorine atom enters the methylene carbon atom adjacent to the keto-group with the formation of the chloroketones of formula (IX). We have actually found that the final sulphanilamidothiazoles (XI) obtained

by both the methods are identical. The compounds obtained by the former procedure immediately yielded crystalline products; but those got by the latter did not crystallise readily which is probably due to the contamination of the chloroketone with isomeric products formed during the chlorination of the ketone. The aminothiazoles (X) in a few cases were also prepared *via* the bromoketones, the final sulphanilamidothiazoles obtained from these were also identical with those obtained by the other methods. Since it is known that in the bromination of the ketones (VII) and ketonic esters (VI) the orientation of the bromine atom depends upon the conditions of the reaction, other conditions are being studied to prepare the bromo-compounds corresponding to the chloro analogues (VIII *a* and IX *a*), with a view to preparing from them 2-amino-4-alkylthiazoles.

Since our immediate interest is only the preparation of the sulphanilamidothiazoles (V and XI) and our stock of chemicals is also very limited, the intermediate new products could not be studied in detail at present but will be done at a later date.

The compounds obtained by the above methods are listed in the table. It may be mentioned that 2-sulphanilamido-5-methylthiazole and 2-sulphanilamido-4,5-dimethylthiazole have been described in a patent of Messrs. May and Baker⁴. The sulphanilamido-alkyl-thiazoles are being tested in many bacterial infections and the results obtained will be reported in due course. If the results are encouraging, further synthesis of more compounds of these groups with higher alkyl groups will be undertaken.

Experimental

2-N¹-Sulphanilamido-5-alkylthiazoles (V)—Since all the compounds were prepared by essentially the same method with but slight alterations in conditions to suit the individual cases, only the general methods are here described.

The aliphatic aldehyde (I) (obtained from the Eastman Kodak Co., Rochester), under external cooling with ice cold water, was gradually treated with 1.1 molecular equivalent of sulphurylchloride. The reaction took place just at about the room temperature (25°–28° C) and when it tended to become vigorous, the mixture was cooled in ice-cold water. After allowing it to stand with frequent shaking for 2–3 hours, it was poured into cold water, the heavy oil separated, washed free from acid with water and boiled with one molecular equivalent of an aqueous solution of thiourea. The boiling was continued till no more of the oil went into solution (usually 2–5 hours). The solution was then thoroughly extracted with ether to remove

any unchanged material and the aqueous clear solution basified with sodium hydroxide when the aminothiazole separated as an oil. This was taken up in ether, the extract dried and the solvent removed, 2-amino-5-alkylthiazole (III) was thus obtained as a mass of crystals in the case of the butyl and amyl derivatives and as a thick syrup in the rest. Without any further purifications, they were condensed with *p*-acetaminobenzenesulphochloride in pyridine medium to yield the acetyl derivatives of formula (IV) which were then hydrolysed smoothly

TABLE

Serial No	Name of Compound	Melting Point °C	Molecular Formula	% NITROGEN	
				Found	Required
	2-Amino-5-amylthiazole	72-73	$C_8H_{14}N_2S$	16.1	16.5
	2-Amino-4-methyl-5-isopropylthiazole	78	$C_{10}H_{16}N_2S$	15.2	15.2
	2-N ¹ -Sulphanilamido-				
87	" 5-ethylthiazole	170	$C_{11}H_{13}N_2O_2S_2$	14.8	14.8
90	" 5-isopropylthiazole	217-18	$C_{13}H_{15}N_2O_2S_2$	14.1	14.1
88	" 5- <i>n</i> -butylthiazole	246	$C_{13}H_{17}N_2O_2S_2$	14.0	13.5
89	" 5- <i>n</i> -amylthiazole	237	$C_{14}H_{19}N_2O_2S_2$	12.6	12.9
80	" 4-methyl-5-ethylthiazole	193-94	$C_{12}H_{15}N_2O_2S_2$	14.4	14.1
73	" 4-methyl-5-propylthiazole	197-98	$C_{13}H_{17}N_2O_2S_2$	14.0	13.5
78	" 4-methyl-5-isopropylthiazole		$C_{13}H_{17}N_2O_2S_2$	13.0	13.5
72	" 4-methyl-5- <i>n</i> -butylthiazole	192-93	$C_{14}H_{19}N_2O_2S_2$	13.5	12.9
74	" 4-methyl-5- <i>n</i> -amylthiazole	187-88	$C_{15}H_{21}N_2O_2S_2$	12.3	12.4
75	" 4-methyl-5- <i>n</i> -hexamylthiazole	202-04	$C_{16}H_{23}N_2O_2S_2$	12.2	12.4
79	" 4-methyl-5- <i>n</i> -heptylthiazole	191-92	$C_{16}H_{23}N_2O_2S_2$	11.9	11.9
	2-N ¹ -Acetsulphanilamido-				
87 Ac	" 5-ethylthiazole	241-42	$C_{13}H_{15}N_2O_4S_2$	13.4	13.0
90 Ac	" 5-isopropylthiazole	200-01	$C_{15}H_{17}N_2O_4S_2$	12.2	12.4
88 Ac	" 5- <i>n</i> -butylthiazole	211-12	$C_{15}H_{19}N_2O_4S_2$	11.9	11.9
89 Ac	" 5- <i>n</i> -amylthiazole	229	$C_{16}H_{21}N_2O_4S_2$	11.0	11.4
73 Ac	" 4-methyl-5- <i>n</i> -propylthiazole	236-38	$C_{15}H_{19}N_2O_4S_2$	11.8	11.9
72 Ac	" 4-methyl-5- <i>n</i> -butylthiazole	216-18	$C_{16}H_{21}N_2O_4S_2$	11.6	11.4
75 Ac	" 4-methyl-5- <i>n</i> -amylthiazole	234-36	$C_{17}H_{23}N_2O_4S_2$	11.3	11.0
79 Ac	" 4-methyl-5- <i>n</i> -hexylthiazole	216-18	$C_{18}H_{25}N_2O_4S_2$	10.8	10.6

to the final 2-sulphanilamido-5-alkylthiazoles (V) with about 4-5 N hydrochloric acid. All the compounds were readily obtained in fine crystalline forms and the overall yields were good in all cases.

2-N¹-Sulphanilamido-4-methyl-5-alkylthiazoles (XI)—The general methods of synthesis of these compounds are as follows—

The alkylbromides (R Br) used in these experiments were all prepared from the corresponding alcohols by the usual sodium bromide-sulphuric acid method. The condensation of the alkylhalides with sodium ethyl acetoacetate to yield the alkylketonic esters (VI) and the hydrolysis of these to the

ketones (VII) were carried out according to methods described in Literature Methylhexylketone was prepared by the oxidation of capryl alcohol

Method 1 —The methylalkylketone (VII), cooled in ice-cold water, was treated gradually with about one molecular equivalent of sulphurylchloride. The mixture was allowed to stand for about two hours or more with frequent shaking, treated with water, the heavy oil that separated was washed with water, dried and fractionated. The first fraction consisted of the unchanged ketone and the higher boiling one was the required chloroketone (IX) which usually collected within a range of 5–10° C (this was not refractionated unless the range was much greater). The chloroketone, thus obtained in yields of 80–90%, was boiled with an aqueous solution of thiourea (one molecular equivalent) till no more of the oil could go into solution (2–4 hours). The cooled solution was thoroughly extracted with ether and the clear acid solution basified with sodium hydroxide. The precipitated thick oil was extracted with ether, the extract dried and the solvent removed whereby the aminothiazole (X) was obtained as a syrup (yield, 50–80%). Without any further purification, this was condensed with *p*-acetaminobenzenesulphochloride in pyridine medium. After allowing the mixture to stand overnight it was warmed on the water-bath for about an hour and on dilution with water, a gummy product was obtained which solidified on vigorous scratching (yield, 50–80%). Further purification of this was effected by dissolving it in ammonia or soda solution (charcoal) and precipitating with hydrochloric acid. The 2-acetsulphanilamido-4-methyl-5-alkylthiazole thus obtained was repeatedly crystallised from isopropyl alcohol. To prepare the 2-sulphanilamido-4-methyl-5-alkylthiazole (XI), the crude acetyl compound was boiled with about ten parts of 4–5 N hydrochloric acid till the solid went into solution (20–60 minutes). In case the hydrochloride separated on cooling, just enough water was added to get a clear solution. After treating it with charcoal, the partly decolourised solution was neutralised when the final product separated as a gum and solidified on scratching (yield, 60–80%). After a few crystallisations from isopropyl alcohol, the 2-sulphanilamido-4-methyl-5-alkylthiazoles (XI) were obtained as colourless or almost colourless crystals. Only the isopropyl derivative, 78, could not so far be obtained as a sharp melting product though it gave the correct analytical figures. According to this procedure, all the compounds except 80 were prepared.

Method 2 —The ketoester (VI) was chlorinated as usual with sulphurylchloride and the resulting chloroester (VIII), obtained in 40–60% yield, was refluxed with a mixture of four parts of 35% sulphuric acid and four

parts of glacial acetic acid for 6-8 hours. The oil obtained on dilution was taken up in ether, the ether extract dried, the solvent removed and the resulting oil fractionated. The chloroketone (IX) thus furnished in yields of 10-40% corresponded in boiling point to that obtained by the previous method. The rest of the procedure in obtaining the final sulphanilamido-thiazoles (XI) was as described under method 1. The products obtained by this method were much purer and crystallised very readily. The sulphanilamidothiazoles (XI) obtained by this and the previous method 1 were identical (there being no depression in melting point). According to this method all compounds excepting compounds 74 and 78 were prepared.

Method 3—The ketone (VII) dissolved in five times the weight of glacial acetic acid and a few drops of hydrobromic acid (48%), under cooling in ice-water, was treated gradually with one molecular equivalent of bromine dissolved in three times the quantity of glacial acetic acid. The decolourisation was immediate and after allowing to stand for about 15 minutes, the solution was poured into cold water, the heavy oil separated, washed free from acid and boiled with one molecular equivalent of thiourea in aqueous solution. The rest of the procedure was as indicated in the previous method 1. According to this method, compounds 72, 73, 74 and 75 were prepared and were found to be identical with the corresponding ones prepared by the foregoing methods.

We express our grateful thanks to Lt-Col S S Sokhey, Director, Haffkine Institute, Bombay, for his keen interest in these investigations.

Summary

In the course of the attempts to study the effects of the different types of substituents in the molecule of 2-N¹-sulphanilamidothiazole, the synthesis of a series of 2-N¹-sulphanilamido-5-alkyl- and 2-N¹-sulphanilamido-4-methyl-5-alkyl-thiazoles, wherein the alkyl group varies from ethyl to hexyl, have been effected and these compounds are described.

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MODIFIED METHODS FOR THE DETERMINATION OF TOTAL ALKALI, SULPHATE, NITRATE AND PHOSPHATE IN HIGHLY COLOURED SOLUTIONS OF HIGH ORGANIC MATTER CONTENT

BY N V R IVENGAR, M Sc, A I C, HON M INST S P.

(Sewage Research Chemist, Ahmedabad Municipality)

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Introduction

DURING the course of investigations on the waste water from factories like, the textile mills, tanneries, dairies and other industrial concerns considerable difficulty was met with for their analysis, owing to the presence of large proportions of suspended as well as dissolved organic matter, and also due to colour of the solution. These effluents in general are highly coloured—the colour ranging from deep black to deep pink. In such cases the routine methods of quantitative determination of the radicles present in the water are not suitable. The volumetric and colorimetric estimations are rendered impossible owing to the high turbidity and the natural colour of the solutions. In the gravimetric analysis, the precipitates are rendered colloidal due to the peptising action of the dissolved organic matter, thus filtration of the precipitates is made difficult. Furthermore, the precipitates adsorb the colour present in the solutions, and thus account for higher results. This difficulty is more prominent in the case of the determination of sulphate. Thus it is clear that solution under examination should be rendered free from colour, and organic matter, so that routine methods for the analysis of such waters may be employed. With this view several ways of destroying the colour as well as the organic matter present in solutions, in order to render the subsequent analysis of the solution easy, were tried and the results obtained are presented in this paper.

Fowler, in his section on "Water and Water Examinations" in the *Technical Methods of Analysis* by Lunge and Keane has referred to the analysis of sulphates and chlorides present in coloured solutions. He¹ suggests that prior to the estimation of sulphates, the organic matter present in the liquid may be destroyed by boiling with 5-10 drops of fuming hydrochloric acid and a few c.c. of strong chlorine-water. The excess of chlorine is boiled

off, the resulting solution cooled and sulphate determined in the usual way. In the same section, Fowler² recommends the use of potassium permanganate for the destruction of colour and organic matter present in the solutions prior to the analysis of chlorides. But it will be seen that these methods are not of universal application

In a previous communication by the author³ it has been shown that hydrogen peroxide may be used with advantage to oxidise the organic matter in order to render the solution colourless, prior to the analysis of chlorides by the usual silver nitrate titration method. The excess of hydrogen peroxide which is left unused is boiled off with a little alkali, and the chloride determined in the usual way. Quite concordant and reliable results have been obtained by this modification of the method. This new procedure has now been extended to the analysis of several of the radicles present in highly coloured and turbid waters, and the details of the methods in each case have been worked out. The results obtained in all the above cases have been presented in the following pages

Experimental

(A) *Determination of total alkali*—For the volumetric determination of the total alkali by the indicator method, it is necessary that the solution under examination should be absolutely colourless, and free from suspended as well as dissolved organic matter. Fowler's methods (*loc cit*) of rendering the solution clear and colourless are unsuitable in these cases since either of his procedures would interfere with the radicles present in the water. The hydrogen peroxide method on the other hand, has been found to be quite useful, and the experimental procedure is as described below.

A known volume (50 c c) of the filtered liquid is transferred into a 250 c c conical flask and heated to boiling. Then 10 per cent hydrogen peroxide (Merck A R redistilled quality free from acids, etc) is added from a burette drop by drop until a faint colouration remains. The contents of the flask are then boiled until the colour gets completely discharged and the evolution of oxygen ceases. The liquid is then cooled, and quickly filtered through paper, all washings being done with freshly boiled distilled water. The resulting colourless and clear solution is titrated against standard acid with methyl orange as indicator and the total alkalinity of the sample is determined. The results are calculated as parts of sodium carbonate per 100,000

Also, parallel determinations were made on solutions of known alkalinity. The results obtained are quite concordant as shown by the following table:

TABLE I
Analysis of Total Alkalinity
(Parts per 100,000)

No	Source of the sample	Description of the sample	Total alkalinity expressed as parts of sodium carbonate per 100,000	
1	<i>Textile Trade Waste Water—</i> (a) Sample I Dye-house waste	Highly turbid, coloured green	133.55	
	(b) Sample II ..	Turbid, coloured black	67.74	
	(c) Sample III Mixed waste	Turbid, coloured brown	66.42	
2	<i>Tannery Waste Water—</i> (a) Sample I	Coloured pale yellow	Trace	
	(b) Sample II	Viscous, pale yellow	2.6	
3	Sample of water from a local tank full of dispersed organic matter	Coloured pale green and highly turbid	3.8	
4	<i>Standard Solutions—</i> (a) 80 parts of NaOH plus 53 parts of Na_2CO_3	Clear and colourless	Sodium hydroxide 79.3	Sodium carbonate 54.0
	(b) 40 parts of NaOH plus 53 parts of Na_2CO_3	..	39.1	53.4

(B) *Sulphate*—The estimation of sulphate in trade wastes was carried out by the method described by Treadwell and Hall⁵. Prior to the determination of the sulphate, the trade waste samples were decolourised by the two methods (1) The Fowler's chlorine-water method and (2) the hydrogen peroxide method described below.

A known volume of the filtered sample of the liquid (100 c.c.) is pipetted into a conical flask and heated to boiling. Then a few c.c.'s of 10 p.c. hydrogen peroxide are added drop by drop until the colour of the solution is almost discharged. The contents of the flask are then boiled for a few more minutes to decompose the excess of hydrogen peroxide. If necessary a few drops of strong sodium hydroxide solution are added to hasten the decomposition of the peroxide. The liquid is then filtered and the sulphate in the filtered liquid determined by precipitating it as barium sulphate.

The same procedure is followed in the determination of the other radioles described in the paper.

The results obtained are presented in Table II.

Parallel determinations of sulphate were carried out with solutions of known sulphate content with a view to test the accuracy of the methods employed. The results of these analysis are also included in Table II.

An examination of Table II shows that the hydrogen peroxide method gives results which are quite reliable and agree with those got by the Fowler's method

TABLE II
Sulphate
(Parts per 100,000)

No	Source of the sample	Description of the sample	Hydrogen peroxide method (Author)	Chlorine-water method (Fowler)
1	<i>Textile Trade Waste Water—</i> (a) Sample I Dye-house waste	Highly turbid, greenish	40 3	40 1
	(b) Sample II „	Turbid, coloured black	22 6	22.85
	(c) Sample III Mixed waste	Turbid, coloured brown	36 45	36 0
2	<i>Tannery Waste Water</i>	Viscous, pale yellow	11 66	12 48
3	<i>Dairy Waste Water</i>	Opalescent	7 40	7 70
4	<i>Sample of water from a local tank</i>	Coloured green and plenty of suspended matter	3 12	3.20
5	<i>Standard Potassium Sulphate solution</i> (a) Containing 126.6 parts of SO_4 soln.	Clear and colourless	126 0	125 6
	(b) „ 63.3 parts of SO_4 soln.	„	63 05	63 0
	(c) „ 31.56 parts of SO_4 soln.	„	31 20	31 35

(C) *Nitrate*.—The proportion of nitrate present in such effluents is not usually high and hence only colorimetric methods are suitable for its determination. As in previous cases the effluents are to be made colourless and clear, before estimation of the nitrates are conducted, as otherwise the original colour of the solutions makes the analysis impossible. A comparative study of Fowler's chlorine-water method and the hydrogen peroxide method (for decolourisation) has been made. The nitrate has been estimated by the phenol disulphonic acid method*. The results are presented in Table III. As before, parallel determinations of nitrate have been made with solutions of known nitrate content and the results are included in Table III.

An examination of Table III shows that the hydrogen peroxide method gives reliable and accurate results. It may also be pointed out that the Fowler's chlorine-water method is elaborate as it invariably involves the precipitation of the chlorides with silver sulphate. The removal of the chlorides is necessary since they interfere in the phenol disulphonic method for the determination of nitrates.

TABLE III
Nitrate Nitrogen
(Parts per 100,000)

No	Source of the sample	Description of the sample	Hydrogen peroxide method (Author)	Chlorine-water method (Fowler)
1	<i>Textile Trade Waste Water—</i> (a) Sample I Dye-house waste	Highly turbid, greenish	16.6	15.8
	(b) Sample II „	Turbid; coloured black	21.1	20.2
	(c) Sample III „	Turbid, coloured brown	7.15	7.01
2	<i>Tannery Waste Water—</i> (a) Sample I	Coloured pale-yellow, viscous	3.02	3.00
	(b) Sample II	„	2.8	2.55
3	<i>Dairy Waste Water—</i> Sample I	Faintly greenish, highly turbid	0.62	0.60
4	Local tank water containing large quantity of dispersed organic matter	Greenish and turbid	0.86	0.89
5	<i>Standard Solution—</i> (a) Containing nitrate nitrogen 10 parts per 100,000	Colourless and clear	9.80	9.82
	(b) Containing nitrate nitrogen 5 parts per 100,000	„	4.82	4.76

(D) *Phosphate*.—The proportions of phosphate present in the effluents under examination have been so low that only the colorimetric methods are suitable for their determination, and the Denige's method modified by Florentin and Atkins' has been found to be quite suitable.

The hydrogen peroxide method for the destruction of colour and organic matter of the solution has been employed. But in this case it is quite necessary that the resulting solution after boiling with hydrogen peroxide should be absolutely free from hydrogen peroxide, as otherwise erroneous results and often negative tests for phosphates are obtained. Thus the resulting solution after filtration is again boiled for sometime with a few drops of phosphate-free alkali, and when the hydrogen peroxide has been completely

decomposed, the solution is cooled, and made up to a known volume and the phosphate determined by the modified Danige's method. The method consists in matching the blue colour produced by the addition of 2 c.c. of molybdic acid solution and 0.5 c.c. of stannous chloride solution to the sample of water under test, with similar solutions of known phosphate content. The results obtained are accurate and the reliability of the method has been found out as before by carrying out a series of determinations with solutions of known phosphate content. The results are as shown in Table IV.

TABLE IV
Phosphate
(Parts per 100,000)

No	Source of the sample	Description of the sample	Hydrogen peroxide method (Author)
1	<i>Textile Trade Waste Water—</i> (a) Sample I Dye-house waste	Highly turbid; greenish	1.62
	(b) Sample II "	Turbid, coloured black	1.25
	(c) Sample III Mixed waste	Turbid, coloured brown	1.36
2	<i>Tannery Waste Water—</i> (a) Sample I	Coloured pale yellow and viscous	6.65
	(b) Sample II	"	5.02
3	<i>Dalry Waste Water</i>	Faintly greenish and turbid	2.03
4	<i>Sample of Tank Water</i>	Greenish and turbid	0.018
5	<i>Standard Sodium Phosphate Solution—</i> (a) Containing 5 parts of PO_4^{3-}	Clear and colourless	4.82
	(b) Containing 2 parts of PO_4^{3-}	"	1.91
	(c) Containing 1 part of PO_4^{3-}	"	1.32

Conclusion

As shown in the foregoing pages the analysis of highly coloured and turbid effluents has been much simplified by the previous oxidation of colour and organic matter by hydrogen peroxide under suitable conditions. It has also been shown that the hydrogen peroxide method is more convenient than the other two methods, namely the permanganate method and the chlorine-water method. The hydrogen peroxide method can moreover be

employed for determination of total alkali, whereas the other two methods are unsuitable

It must however be conceded that the bicarbonate, the nitrite and sulphite, escape determination by any of the above methods since all of them are decomposed during the pre-treatment of the effluents under analysis. While the bicarbonates get precipitated as their carbonates during the course of pretreatment and thus are removed out of the solution during the subsequent filtrations, nitrite and sulphite are oxidised to nitrate and sulphate respectively, thus adding to proportions of nitrate and sulphate already present. Further work on this aspect of the problem is in progress

The estimation of stable radicles in turbid and highly coloured fluids can be conveniently conducted after the pretreatment with hydrogen peroxide. It may be confidently hoped that this method will find a wide application in the biological analysis of highly coloured liquids of biological origin

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THE COLOURING MATTER OF THE FLOWERS OF *TAGETES PATULA*: ISOLATION OF A NEW FLAVONOL, PATULETIN AND ITS CONSTITUTION

BY P SURYAPRAKASA RAO AND T R SESHADRI
(From the Department of Chemistry, Andhra University, Waltair)

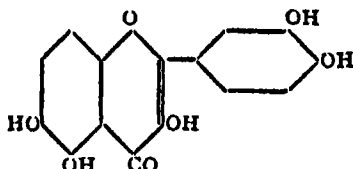
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Tagetes patula, the French Marigold (called *Seemabanthi* in Telugu) is similar to *Tagetes erecta*, except that it has a bushy and spreading habit. The flowers are much smaller in size, but borne in larger numbers. In colour they are red tinted and variegated. They do not seem to have been investigated before. It has been recently pointed out by us¹ how De La Source and Perkin on the one hand and Mahal on the other, thought that they were dealing with the two different species, but actually examined one and the same species *Tagetes erecta*. The confusion arose from a wrong combination of the botanical and the common names.

A genuine sample of the flowers of the *patula* was collected and examined according to the general method already outlined in some of our past publications.² The concentrated alcoholic extract of the petals did not deposit any solid even after several days but on dilution with water, a pale yellow crystalline substance separated out in good yield. After the removal of this solid, the mother-liquor was successively treated with neutral and basic lead acetate solutions, when an orange-red precipitate was produced in each case. The aqueous solution obtained by the decomposition of the neutral lead acetate precipitate did not yield any solid even after six months. It, however, contained a glucoside and on hydrolysis produced glucose and an aglucone which was found to be identical with the yellow substance obtained by the dilution of the original alcoholic concentrate. The glucoside itself could not be obtained and experiments are being carried out to effect its isolation. The basic lead acetate fraction was not much and was therefore, discarded.

The pale yellow crystalline solid isolated as given above is found to be a new pigment, and is named "Patuletin", as it has been obtained from the flowers of the *patula*. It has the elementary formula $C_{18}H_{16}O_7$ and melts at 262–64°. On treatment with lead acetate it gives a deep red precipitate, and in 50% alkali it undergoes ready oxidation in the cold, thereby indicating that it is a flavonol. The substance yields a pentaacetyl derivative and a pentamethyl ether, and hence it should be a tetrahydroxy flavonol. It is, therefore, isomeric with quercetin and herbacetin. As a result of oxidation in alkaline solution, it yields protocatechuic acid, which could be isolated

after methylation, in the form of veratric acid. So the flavonol contains two hydroxyl groups in the 3' and 4' positions. Since the naturally occurring hydroxy flavones and flavonols with the exception of one or two invariably contain a hydroxyl group in position 5, it is very likely that the new substance does not add yet another member to the exceptions to the general rule, and hence it may be presumed that one of the two hydroxyl groups in the benzopyrone ring is in position 5. For the other hydroxyl therefore, one of the remaining three positions 6, 7 and 8 is available. It does not seem to be present in position 8, as the substance is not oxidised by *p*-benzoquinone to give the "gossypetone" reaction (*cf* cannabiscetin³). Nor can it be in position 7, as the compound is not identical with quercetin. Hence patuletin is tentatively represented as 3·5·6·3'·4'-pentahydroxy flavone



In further support of the above structure, it may be pointed out that the flavonol present in the closely allied species *T. erecta* has two hydroxyl groups in 5 and 6 positions (quercetagetin). The resemblance between patuletin and quercetagetin is very close in regard to many of their reactions. Like the latter the new flavonol immediately dissolves in alkali forming yellow solutions. When treated with a drop of ferric chloride, an alcoholic solution of the substance produces a greenish brown colour. With alkaline buffer solutions, as in the case of quercetagetin, no prominent colour changes are produced. When treated with sodium amalgam (Bargellini's test), patuletin immediately yields bluish green flocks, but the colour changes to almost pale yellow in about ten minutes and remains so even after 48 hours. By the action of diazomethane, the pigment undergoes complete methylation. This may be counted as evidence against the existence of a hydroxyl group in the 5th position. But the objection cannot be valid since quercetagetin itself is completely methylated under the same conditions⁴. The resistance of the hydroxyl group in position 5 to methylation seems to be dependent on the disposition of other hydroxyls in the ring and to be greatest when they are present in the 5-7-8 combination as in herbacetin⁵ and gossypetin.⁶

Support for the suggested structure of patuletin is expected to be obtained from synthesis which is in progress.

Experimental

Isolation of Patuletin.—The dry petals (1,000 g) of the flowers of *Tagetes patula* were extracted twice with boiling alcohol, each extraction

lasting over 12 hours, and the extract concentrated to about 300 c.c. After filtering through fluted filters the resins and the waxes that separated out, the clear concentrate was allowed to stand for a month, but no solid was deposited. It was, therefore, diluted with a large volume of water (1,500 c.c.), when a yellow crystalline solid began to precipitate out. The next day it was filtered and washed with water. As it was still impure and sticky, it was dissolved in a little pyridine and water was added to the solution till the impurities separated out as a suspension. They were coagulated by the addition of calcium chloride and filtered off. The clear filtrate which did not develop any more turbidity on further dilution was concentrated till the pigment separated out as yellow needles. Further purification of the substance was effected by crystallisation twice from alcohol, when it came out as clusters of dull yellow needles sintering at 260° and melting at 262–64°. It was sparingly soluble in water but easily dissolved in pyridine, alcohol and acetic acid. (Found in air-dried sample C, 53.5; H, 4.4, $C_{15}H_{10}O_7 \cdot 2H_2O$ requires C, 53.5, H, 4.1%. Found in the sample dried at 120° *in vacuo* C, 59.4, H, 3.5, $C_{15}H_{10}O_7$ requires C, 59.6, H, 3.3%.) On acetylation with acetic anhydride and anhydrous sodium acetate, the pigment yielded a pentaacetyl derivative melting at 170–72°. It crystallised from dilute acetic acid as clusters of colourless needles. [Found C, 58.1, H, 3.9, $C_{15}H_5O_2 (OCOCH_3)_5$ requires C, 58.6, H, 3.9%]

The Neutral Lead Acetate Fraction—The aqueous solution left after the removal of the new flavonol was treated with excess of neutral lead acetate. The orange red precipitate produced was filtered, washed, suspended in water and decomposed with hydrogen sulphide. The aqueous solution thus obtained was concentrated and left aside after the addition of a few drops of toluene. Even after six months no pigment separated out but a small amount of resin settled down. The clear liquor was extracted with ether and the extract yielded a small amount of patuletin on evaporation. To see if the aqueous solution contained any glucosides, it was made 7% acid by the addition of the calculated amount of concentrated sulphuric acid and boiled under reflux. In about fifteen minutes some brown solid separated giving rise to bumping, and the subsequent heating had to be carried out on a boiling water-bath. After two hours, the contents were cooled and filtered. A portion of the filtrate was neutralised with barium carbonate, concentrated to a small bulk and then treated with phenyl hydrazine in acetic acid solution, when an osazone was produced. This was identified as glucosazone melting at 204–06°. The solid residue was brown in colour and it was contaminated with a considerable amount of resin, which could not be removed by direct crystallisation. So the mixture was macerated with cold alcohol when all the brown resin went into solution leaving most of the pigment

behind. By this treatment and subsequent crystallisation from fresh alcohol, it was obtained as clusters of yellow needles melting at 260–62°. It was identified as the new flavonol, patuletin, from a study of its properties and the comparison of the acetyl derivatives

Properties of Patuletin—The substance was not a glycoside since it remained unaffected, when boiled with 7% sulphuric acid for two hours. It very easily dissolved in alkalis producing orange-yellow solutions. Ferric chloride imparted a brownish green colour to an alcoholic solution of the substance. When a small amount of sodium amalgam was added to a solution of the substance in absolute alcohol, bluish green flocks were immediately produced, but their colour changed to almost pale yellow in about 10 minutes and remained so even after 48 hours. Neutral lead acetate produced a deep red precipitate, when added to an alcoholic solution of the pigment. When a solution of the substance in absolute alcohol was treated with *p*-benzoquinone, the original colour of the solution did not change, nor did any solid separate out even after several days. The colour reactions of the flavonol with alkaline buffer solutions were not prominent. In this and most of the other properties given above, it resembled quercetagetin closely.

Alkaline Oxidation of the Flavonol Isolation of Veratric Acid.—The flavonol (1 g) was treated with 50% aqueous potash (20 c.c.) when it dissolved immediately to form an orange-yellow solution. On leaving exposed to air with occasional shaking for 24 hours, the solution became opaque and brown. It was then diluted, and treated with excess of dimethyl sulphate (20 c.c.) in small quantities. After shaking for an hour, the contents were heated on a water-bath for about 30 minutes to complete the methylation and decompose the excess of the dimethyl sulphate. The clear alkaline solution was then acidified, and extracted with ether, when a colourless crystalline acid was obtained. It crystallised from alcohol in the form of needles melting at 183–84° and was found to be identical with veratric acid.

Preparation of Pentamethyl Patuletin—(a) Pentaacetyl patuletin (0.5 g.) was dissolved in acetone (20 c.c.) and treated in small quantities alternately with dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.). Subsequently further quantities of dimethyl sulphate (5 c.c.) and alkali (5 c.c.) were added, and finally the medium was made definitely alkaline by the gradual addition of more alkali (15 c.c.). After leaving overnight, the mixture was refluxed for half an hour to complete the methylation. When the excess of the solvent was distilled off, a yellowish white substance was produced. It was recrystallised from dilute acetic acid using a little animal charcoal, when it appeared as colourless needles and narrow rectangular plates.

(b) The flavonol (1 g) was dissolved in anhydrous methyl alcohol (50 c.c.) and then treated in small quantities during two days with excess of diazomethane (3 g) in ether solution. After each addition, the mixture assumed an orange colour which gradually faded on subsequent shaking. After the completion of the reaction, the ether and the excess of diazomethane were driven off on a water-bath, when a brown solid was left behind. On crystallisation from alcohol using a little animal charcoal, the ether was obtained as colourless narrow rectangular plates.

The two samples of the ether as obtained by the above methods were found to be identical. The pure substance sintered at about 143° and melted completely at 158–59° [Found OCH_3 , 39.6, $\text{C}_{18}\text{H}_{15}\text{O}_2 (\text{OCH}_3)_6$, H_2O requires OCH_3 , 39.7%]

Alkaline Oxidative Hydrolysis of Pentamethyl Patuletin.—The Pentamethyl ether (1 g) was refluxed in a silver flask with 50% potash (20 c.c.) for 6 hours, at the end of which it was completely disrupted. The clear alkaline solution on acidification did not precipitate any solid. When extracted with ether, however, and when the ether solution was evaporated, a crystalline solid was obtained and was found to be identical with veratric acid melting at 182–84°

Summary

A new flavonol, patuletin has been isolated from the petals of the flowers of *Tagetes patula* (French Marigold). It contains five hydroxyl groups and yields a pentaacetate and a pentamethyl ether. It is, therefore, isomeric with quercetin and herbacetin. On oxidation in cold alkali, the substance decomposes into protocathechuic acid which could be isolated after methylation as veratric acid. The completely methylated ether also yields veratric acid on boiling with potash. Assuming that a hydroxyl group is present in position 5, as is the case with most of the naturally occurring flavones and flavonols, the remaining hydroxyl group in the compound is concluded to be in position 6 in view of the properties of the flavonol and its resemblance to quercetagetin. Hence patuletin is represented as 3, 5, 6, 3', 4'-pentahydroxy flavone

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FINITE STRAIN IN A ROTATING SHAFT

BY B. R. SETH

(From the Department of Mathematics, Hindu College, Delhi)

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THE theory of finite strain in elastic problems has been developed on the hypothesis that we do not neglect the second order terms in the components of strain ^{1,2} Some applications of it have been given in recent papers ^{3,4-6} When applied to the case of a solid rotating shaft we get an exact solution of the stress equations of equilibrium, and the comparison of the results with those given by the small strain theory becomes quite interesting.

We treat the problem as one of plane strain, with an allowance for uniform longitudinal extension, α Since the shaft is strained symmetrically we can take the components of displacement as

$$u = x(1 - \beta), v = y(1 - \beta), w = \alpha z, \quad (1)$$

where β is a function of $r = (x^2 + y^2)^{\frac{1}{2}}$ only.

The stress components are given by

$$\widehat{xx} = \lambda\delta + \mu \left[(1 - \beta^2) - x^2 \left(\beta'^2 + \frac{2\beta\beta'}{r} \right) \right], \quad (2.1)$$

$$\widehat{yy} = \lambda\delta + \mu \left[(1 - \beta^2) - y^2 \left(\beta'^2 + \frac{2\beta\beta'}{r} \right) \right], \quad (2.2)$$

$$\widehat{zz} = \lambda\delta + \mu (2\alpha - \alpha^2), \quad (2.3)$$

$$\widehat{yz} = \widehat{zx} = 0, \quad (2.4)$$

$$\widehat{xy} = -\mu xy \left(\beta'^2 + \frac{2\beta\beta'}{r} \right), \quad (2.5)$$

where

$$\beta' = d\beta/dr, \text{ and}$$

$$\delta = 1 - \beta^2 - \frac{1}{2} (r^2 \beta'^2 + 2r\beta\beta') + \alpha - \frac{1}{2} \alpha^2 \quad (3)$$

In polar co-ordinates these stresses are given by

$$\widehat{rr} = \lambda\delta + \mu [1 - (r\beta' + \beta)^2], \quad (4.1)$$

$$\widehat{\theta\theta} = \lambda\delta + \mu (1 - \beta^2), \quad (4.2)$$

$$\widehat{r\theta} = \widehat{rz} = \widehat{\theta z} = 0, \quad (4.3)$$

with \widehat{zz} given by (2.3).

The only stress-equation of equilibrium which is not identically satisfied is given by

$$\frac{\partial \widehat{rr}}{\partial r} + \frac{\partial \widehat{rz}}{\partial z} + \frac{\widehat{rr} - \widehat{\theta\theta}}{r} + \rho r \omega^2 = 0, \quad (5.1)$$

which, on substituting from (4), reduces to

$$\frac{\partial}{\partial r} \left[\beta^2 + (r\beta' + \beta)^2 + c \int r\beta'^2 dr - \frac{c}{2\mu} \rho r^2 \omega^2 \right] = 0,$$

where

$$c = \frac{2\mu}{\lambda + 2\mu} = \frac{1 - 2\eta}{1 - \eta},$$

and ω is the angular velocity of the shaft

Since η , the Poisson's ratio, lies between 0 and $\frac{1}{2}$, c lies between 0 and 1.

The differential equation satisfied by β is therefore

$$\beta^2 + (r\beta' + \beta)^2 + c \int r\beta'^2 dr - \frac{c}{2\mu} \rho r^2 \omega^2 = K_1, \quad (5.2)$$

K_1 being a constant.

The general solution involving one arbitrary constant can be obtained in the form of an infinite series. In the present paper we propose to discuss only the particular solution obtained from (5.2) by putting $K_1 = 0$. This is easily seen to be

$$\beta = Ar = \frac{c \rho \omega^2 r}{\mu (10 + c)}. \quad (6)$$

The radial displacement is therefore given by

$$U = r \left(1 - \frac{c \rho \omega^2 r}{\mu (10 + c)} \right). \quad (7)$$

The boundary condition over the curved surface is $\widehat{rr} = 0$ over $r = a$, being the radius of the shaft in the strained condition. Using (4.1) we get

$$(3 - 2c) - (1 - c)(1 - a)^2 = a^2 A^2 (5 - c). \quad (8)$$

The boundary condition over the plane ends is $\widehat{zz} = 0$ over $x = \pm l$, $2l$ being the length of the shaft. This cannot be exactly satisfied. But we can make the resultant longitudinal tension vanish over the plane ends. This requires

$$\int_0^l r \widehat{zz} dr = 0, \quad (9.1)$$

which gives

$$(3 - 2c) - (1 - a)^2 = \frac{1}{4} a^2 A^2 (1 - c). \quad (9.2)$$

We have now the three equations (6), (8), (9 2) to determine the two constants A and a . This implies an identical relation between ρ , a and ω . This is the natural consequence of the fact that (6) is only a particular solution, and not the general solution

The constants a and A are given by

$$(1-a)^2 = \frac{(3-2c)(5+3c)}{5+8c-5c^2}, \quad (10.1)$$

$$A^2 a^2 = \frac{2c(3-2c)}{5+8c-5c^2}, \quad (10.2)$$

and the identical relation is given by

$$\rho a^2 \omega^2 = \frac{2\mu(3-2c)(10+c)}{5+8c-5c^2} \quad (10.3)$$

The non-vanishing stresses are now given by

$$\widehat{rr} = \frac{5-c}{10+c} \rho \omega^2 (a^2 - r^2), \quad (11.1)$$

$$\widehat{\theta\theta} = \frac{\rho \omega^2}{10+c} [a^2(5-c) - r^2(5-4c)], \quad (11.2)$$

$$\widehat{zz} = \frac{5\rho\omega^2(1-c)}{2(10+c)} (a^2 - 2r^2). \quad (11.3)$$

If \widehat{rr}_0 , $\widehat{\theta\theta}_0$, \widehat{zz}_0 , denote the corresponding stresses of the small strain theory, we have¹⁰

$$\widehat{rr}_0 = \frac{1}{2} (4-c) \rho \omega^2 (a^2 - r^2), \quad (12.1)$$

$$\widehat{\theta\theta}_0 = \frac{1}{2} \rho \omega^2 [a^2(4-c) - r^2(4-3c)] \quad (12.2)$$

$$\widehat{zz}_0 = \frac{1}{4} (1-c) \rho \omega^2 (a^2 - 2r^2) \quad (12.3)$$

If a_0 is the corresponding value of a_1 we have for ω given by (10.3),

$$a_0 = -\frac{1}{2} \frac{(1-c)(10+c)}{5+8c-5c^2} \quad (13)$$

Instead of making the resultant longitudinal tension vanish we can suppose that the tension is adjusted on the plane ends so that the length is maintained constant. In such a case $a = 0$, and the identical relation (10.3) takes the form

$$\rho a^2 \omega^2 = \frac{\mu(2-c)(10+c)}{c(5-c)} \quad (14)$$

\widehat{rr} , $\widehat{\theta\theta}$ retain the form given in (11), but \widehat{zz} and \widehat{zz}_0 become

$$\widehat{zz} = \frac{\rho \omega^2 (1-c)}{(2-c)(10+c)} [2(5-c)a^2 - 5(2-c)r^2], \quad (15.1)$$

$$\widehat{zz}_0 = \frac{\rho \omega^2 (1-c)}{4(2-c)} [(4-c)a^2 - 2(2-c)r^2]. \quad (15.2)$$

If U_0 is the radial displacement of the small strain theory, we have¹⁰

$$U_0 = \frac{\rho \omega^2 r}{16\mu(3-2c)} [(2-c)(1+2c)a^2 - c(3-2c)r^2]. \quad (16)$$

If r_1 and r_{10} are the values of r for which U and U_0 vanish, we have

$$\frac{r_1}{r_{10}} = \left[\frac{(5+8c-5c^2)}{2(2-c)(1+2c)} \right]^{\frac{1}{2}}. \quad (17)$$

Since $0 < c < 1$, this ratio lies between 1.118 and 1.155. For $\eta = \frac{1}{4}$ ($c = \frac{2}{3}$), the difference can be as much as 12 per cent.

In like manner we find that (a/a_0) lies between 1 and 0.732. For $\eta = \frac{1}{4}$, the difference between the two values is about 10 per cent.

For comparing the stresses we find

$$\frac{\bar{r}r}{\bar{r}r_0} = \frac{8(5-c)}{(10+c)(4-c)}, \quad (18.1)$$

$$\frac{\bar{z}z}{\bar{z}z_0} = \frac{10}{10+c}. \quad (18.2)$$

The ratio in the first case varies between 1 and 0.97, and in the second case between 1 and 0.91. For the cross-radial stress we find that $(\bar{\theta}\theta/\bar{\theta}\theta_0)$ lies between 1.2 and 0.97.

It appears that, though the stresses given by the two theories are similar in form, the radial displacements have not the same character. Also, the mistake involved in using the small strain theory can be as much as 10 to 12 per cent.

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DECOMPOSITION OF HYDROGEN PEROXIDE BY SODIUM NITROPRUSSIDE

BY BIJAN BIHARI LAL

(From the Chemical Laboratory, Lucknow University)

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QURESHI (1931) pointed out that the decomposition of hydrogen peroxide by sodium nitroprusside in visible light is followed by a marked photochemical after-effect. The reaction in the unilluminated mixture was found to be exceedingly slow, but the decomposition in the pre-illuminated mixture was observed to follow the unimolecular law. He suggested that the after reaction is due to colloidal Prussian blue formed from nitroprusside during irradiation. Preliminary experiments conducted by the present author showed that although the dark decomposition is very slow, the reaction in the pre-insolated mixture is not unimolecular. An attempt was, therefore, made to investigate this after-effect, and to ascertain the nature and the rôle of the catalyst, which is responsible for the non-cessation of the reaction after cutting off the illumination. The photochemical after-effect in $\text{H}_2\text{O}_2\text{-K}_4\text{Fe(CN)}_6$ reaction has been shown by the author (1939) to be due to the photo-formation of potassium aquopentacyanoferrite. It was of interest to examine whether the after-effect in the above reaction might also be traced to a similar cause.

In view of the meagre experimental work on this reaction, it was thought desirable to take up an exhaustive investigation of the problem and try to elucidate the chemical mechanism of the after-effect. Experiments have been conducted with —

- (i) pre-insolated H_2O_2 -nitroprusside reaction mixture;
- (ii) pre-insolated sodium nitroprusside added to hydrogen peroxide in the dark,
- (iii) end solutions of pre-insolated H_2O_2 -nitroprusside mixtures added to fresh hydrogen peroxide in the dark

All the experiments were carried out at 35°C . The volume of the reaction mixture was 50 c.c. in all cases, and the strength of hydrogen peroxide was N/10. The velocity constants have been calculated from the usual unimolecular formula, $K = 1/t \log a/a-x$, where 't' is the time in minutes,

and ' $a-x$ ' is the concentration of H_2O_2 in terms of c.c. of $KMnO_4$ at time ' t '

Photochemical After-effect

The dark reaction is negligibly slow. Sodium nitroprusside (0.0200 gm) dissolved in conductivity water was added to the calculated amount of hydrogen peroxide and the mixture was made up to 100 c.c. It was insulated and when the evolution of oxygen became marked, it was transferred to the dark room. The reaction in this mixture was found to be autocatalytic. It has been observed in connection with another investigation that the decomposition of hydrogen peroxide by sodium aquopentacyanoferrate follows an autocatalytic course, but fairly uniform unimolecular velocity constants are obtained in presence of a suitable excess of potassium ferrocyanide. It was consequently of interest to see if the addition of potassium ferrocyanide to the insulated mixture could give uniform values of the unimolecular constant.

In order to study the effect of potassium ferrocyanide, 100 c.c. of the reaction mixture was insulated as above. It was then divided into 50 c.c. portions and kept in the thermostat. The reaction in the first portion was followed as usual. The other portion of the insulated mixture was treated with the requisite amount of potassium ferrocyanide. The mixture was allowed to stand in the thermostat until all the ferrocyanide had dissolved, and then the decomposition of hydrogen peroxide was followed volumetrically. The amount of permanganate taken up by ferrocyanide was allowed for (by subtraction) from the total volume used in each titration.

TABLE I

Without $K_4Fe(CN)_6$

t	$a-x$	$K \cdot 10^3$
0	13.45	
23	11.50	296
61	7.70	397

TABLE II

With $K_4Fe(CN)_6 = 0.1320$ gm

t	$a-x$	$K \cdot 10^4$
0	9.20	
10	6.90	125
15	5.80	134
24	4.50	129
35	3.50	120
54	1.90	127
72	1.10	128

It is evident that in the absence of ferrocyanide, the reaction shows an autocatalytic course and the velocity constants calculated by the unimolecular formula increase with the progress of the reaction. In the presence of an excess of ferrocyanide, however, constants are obtained for the

unimolecular formula Their absolute values are also much higher than when no ferrocyanide is used

After-effect with Pre-insolated Nitroprusside added to H_2O_2 in the Dark

Experiments were performed with pre-insolated nitroprusside added to hydrogen peroxide in the dark. Sodium nitroprusside (0.2500 gm.) was made up to 500 c.c. in conductivity water and insolated in bright sunlight, until a pale brownish yellow colour appeared. This did not take more than 7 to 10 minutes. The solution was removed to the dark before any blue tint could be noticed. The volume of this solution used in the following experiments was 20 c.c. (0.0100 gm.) (See Table III)

The unimolecular velocity constants are seen to increase with time. The effect of ferrocyanide in varying quantities was next investigated and the following results were obtained. The volume of pre-insolated nitroprusside was 20 c.c. in each case.

TABLE III

t	$a-x$	$K \cdot 10^3$
0	15.00	
60	14.80	97
128	14.60	105
230	14.15	110
310	13.70	127
418	13.15	137

TABLE V

$K_4Fe(CN)_6 = 0.0132 \text{ gm.}$

t	$a-x$	$K \cdot 10^3$
0	14.40	
43	11.70	210
75	10.20	200
99	9.15	199
209	5.65	194
295	4.55	170
356	3.90	159

TABLE IV

$K_4Fe(CN)_6 = 0.0060 \text{ gm.}$

t	$a-x$	$K \cdot 10^3$
0	14.35	
42	13.00	1020
76	12.45	812
108.5	11.95	732
134	11.80	634
210	10.95	559
293	10.05	528
354	9.45	512

TABLE VI

$K_4Fe(CN)_6 = 0.0396 \text{ gm.}$

t	$a-x$	$K \cdot 10^3$
0	13.75	
20	10.25	638
60	6.10	588
83.5	4.30	605
101.5	3.10	637

For the sake of brevity, the other tables are not reproduced, but the results have been summarised below and illustrated in Fig. 1, curve 'a'.

The after-effect has been calculated by subtracting the dark rate of uninso-lated nitroprusside-ferrocyanide-hydrogen peroxide mixture from the rate of pre-insolated nitroprusside-ferrocyanide-hydrogen peroxide mixture.

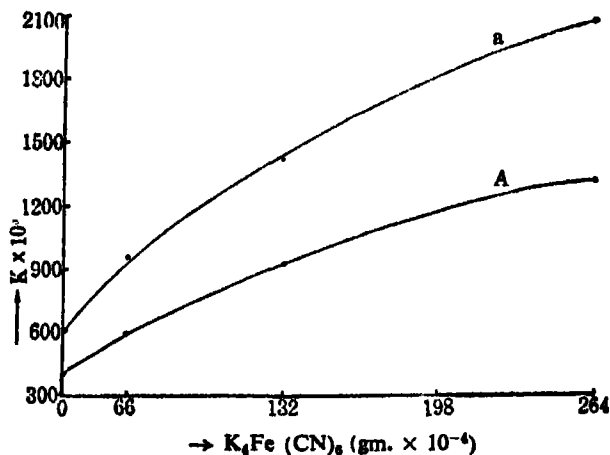


FIG. 1

TABLE VII

$K_4Fe(CN)_6$ used in gm	After-effect $K \times 10^4$
0 0060	Decreasing rate
0 0132	do
0 0396	609
0 0660	957
0 1320	1415
0 2640	2079

The above results show that in presence of an excess of ferrocyanide, not only are uniform values of unimolecular velocity constants obtained, but their absolute values are very much higher than those obtained in experiments in which no ferrocyanide is added. Moreover, the greater the amount of ferrocyanide added, the higher is the velocity constant. When very small amounts of ferrocyanide (0 0060 gm, 0 0132 gm) are used, the velocity constants show a falling off with time. This result is strikingly similar to that observed in ferrocyanide-hydrogen peroxide reaction from the view-point of the photochemical after-effect. The pre-insolated nitroprusside solution does not show any colour change with dilute sulphuric acid, *p*-nitrosodimethylaniline, or nitrosobenzene. But when ferrocyanide is added to pre-insolated nitroprusside solution containing any of the above reagents, very characteristic colour changes are produced in the dark. The first two reagents give a green colouration while the third reagent, *i.e.*, nitrosobenzene, gives a violet colouration. These tests are not given by un-insolated nitroprusside to which ferrocyanide has been added in the dark.

Effect of Concentration Change on Pre-insolated Nitroprusside with Constant Concentration of Ferrocyanide

The results obtained by employing varying quantities of pre-insolated nitroprusside solution with a constant amount (0 0660 gm.) of ferrocyanide have been summarised below and illustrated in Fig. 2, curve 'b'. The

details of one experiment, using 1 c.c of pre-insolated nitroprusside (0.0005 gm) are given below.

TABLE VIII

Pre-insolated nitroprusside
1 c.c (0.0005 gm)

<i>t</i>	<i>a-x</i>	<i>K</i> 10 ³
0	14.10	
22	13.05	153
50	11.80	155
126	9.55	134
154	8.75	135
181	8.10	133
209	7.40	134

TABLE IX

Nitroprusside in gm.	After-effect • <i>K</i> 10 ³
0.0005	148
0.0015	279
0.0025	432
0.0050	650
0.0100	957
0.0150	1157
0.0200	1337

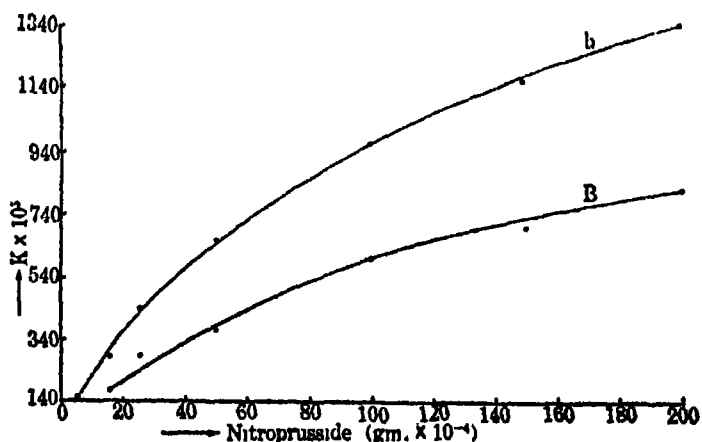


FIG 2

The concentration of ferrocyanide being kept constant, the velocity constants depend upon the amount of pre-insolated nitroprusside. The greater the concentration of pre-insolated nitroprusside, the higher is the value of the velocity constant. Potassium ferrocyanide has been employed in considerable excess in the above experiments.

The following experiment shows the effect of potassium ferricyanide on the reaction mixture of hydrogen peroxide and pre-insolated nitroprusside. The concentration of ferricyanide was the same as that of ferrocyanide, i.e., $M/320$, and the amount of pre-insolated nitroprusside was 20 c.c., i.e., 0.0100 gm.

TABLE X

<i>t</i>	<i>a-x</i>	<i>K</i> 10 ⁵
0	14 95	
16	14 60	64
61	13 40	78
121 5	7 00	271
181	1 80	508
211	0 85	590

The effect of ferrocyanide (in increasing and keeping constant) on the unimolecular velocity constants is quite specific, as ferricyanide does not regulate the reaction. The obvious conclusion is that the catalyst, formed from nitroprusside on insolation, is changed to a more reactive substance by interaction with ferrocyanide and is kept at a constant concentration when the latter is used in excess. Potassium ferricyanide does not show this behaviour.

Diminution in the Reactivity of Pre-insolated Nitroprusside

The catalyst formed by insolation of nitroprusside is fairly stable, as by heating the pre-insolated solution to about 90° C for a few minutes before mixing with hydrogen peroxide-ferrocyanide mixture, the same rate of decomposition is obtained as with the unheated solution. Moreover, a pre-insolated solution of nitroprusside continues to give the same rate of decomposition even many days after insolation. But a very striking change was observed when a mixture of ferrocyanide and pre-insolated nitroprusside was heated to about 90° C for a few minutes before adding to hydrogen peroxide. The value of the velocity constant (*K* 10⁵) comes down from 4450 to about 250. It is significant that pre-heated ferrocyanide, when added to pre-insolated nitroprusside, does not show this tremendous diminution in the catalytic activity. It is evident, therefore, that the catalyst obtained by irradiation of nitroprusside is comparatively stable towards heat, but the more reactive substance formed by interaction of pre-insolated nitroprusside and ferrocyanide in the dark is destroyed by heating the mixture to 90° C. This change was also observed when ferrocyanide-pre-insolated nitroprusside mixture was kept in the dark at room temperature (30° C) for 48 hours before the experiment. The product of interaction between ferrocyanide and the catalyst formed in pre-insolated nitroprusside thus undergoes a slow spontaneous change in the dark with a concomitant diminution in its catalytic activity. The reactivity of pre-insolated nitroprusside in the presence of ferrocyanide is much suppressed by cyanide ions. The after-effect due to the pre-insolated nitroprusside is almost completely 'quenched'.

by sodium nitrite also. The strength of potassium cyanide was N/400 and that of sodium nitrite, N/100. Sodium nitrite was added to pre-insolated nitroprusside and ferrocyanide and this mixture was added to hydrogen peroxide. The excess of nitrite had reacted with hydrogen peroxide before the first reading was taken, and consequently no allowance for nitrite in the titrations was necessary. The effect of heat, standing in the dark for 48 hours, cyanide ions and sodium nitrite is recorded in Tables XI, XII, XIII and XIV respectively. The curves A, B and C in Fig. 3 illustrate

TABLE XI

t	$K \cdot 10^6$
0	
20	261
61	208
108	184
138	176

TABLE XII

t	$K \cdot 10^6$
0	
25	244
60	205
196	160

TABLE XIII

t	$K \cdot 10^6$
0	
30	203
120	153
188	148
205	147
310	169

TABLE XIV

t	$a-x$	$K \cdot 10^6$
0	14.60	
30	14.45	150
60	14.30	152
117	14.10	130
185	13.60	167
255	13.20	172

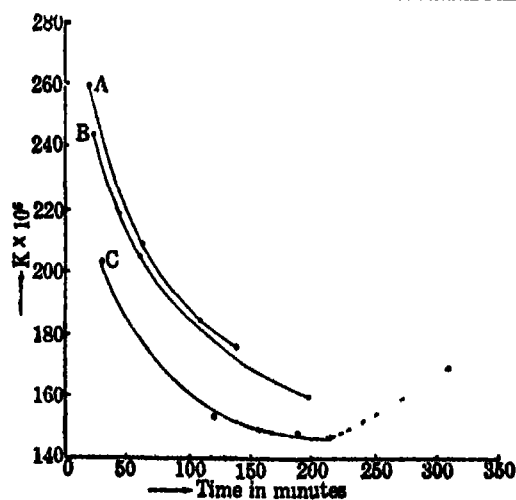


FIG. 3

N.B.—The unisolated nitroprusside-ferrocyanide mixture gives constant values ($K \cdot 10^6 = 126$).

the respective effect of heat, spontaneous change in the dark after 48 hours and lastly of cyanide ions

The control experiment between unisolated nitroprusside (0.0025 gm. and ferrocyanide (0.0660 gm) gave constant values of unimolecular velocity constant, $K \cdot 10^4 = 126$. The same value of K is obtained when no nitroprusside is used. When potassium cyanide (N/400) was employed together with the above two reactants in the dark, the course of the reaction became autocatalytic, probably due to the alkali obtained from potassium cyanide by hydrolysis. It is clear that the velocity constants obtained above tend to approach the values obtained in the control

Secondary After-effect

The effect of adding fresh hydrogen peroxide in the dark to the end solution of pre-insolated nitroprusside-hydrogen peroxide mixture has been called the secondary after-effect (*cf* MacMahon and Lal, 1940). It has been studied by restoring in the dark the hydrogen peroxide used up in the insolated mixture. A mixture (500 c.c.) of hydrogen peroxide (N/10), and nitroprusside (0.2500 gm) was prepared and insolated, until the evolution of oxygen became marked. It was then brought back to the dark room, and allowed to stand until all hydrogen peroxide was decomposed. This end solution was taken in measured quantities and the reaction performed by adding fresh hydrogen peroxide to restore the original strength (N/10) (See Table XV)

The end solution, when added to fresh hydrogen peroxide in the dark, shows an autocatalytic course similar to that observed with pre-insolated nitroprusside. The effect of ferrocyanide in varying amounts was studied on this mixture as well. The amount of the end solution used in each case was 20 c.c. (0.0100 gm).

TABLE XV
End solution = 20 c.c.

<i>t</i>	<i>a-x</i>	$K \cdot 10^4$
0	14.70	.
55	14.55	80
116	14.10	156
175	13.70	175
236	12.95	233

TABLE XVI
 $K_4Fe(CN)_6 = 0.0132 \text{ gm.}$

<i>t</i>	<i>a-x</i>	$K \cdot 10^4$
0	14.10	
13	12.95	284
39	11.90	184
72.5	10.85	157
107	9.80	148
140	8.95	141
176.5	8.20	133
243	7.10	123
278	6.60	119

The other results are summarised below (Table XVIII) The after-effect has been calculated by subtracting from the total rate the dark rate with unisolated nitroprusside and ferrocyanide in each case

TABLE XVII

$K_4Fe(CN)_6 = 0.0396 \text{ gm}$

t	$a-x$	$K \cdot 10^6$
0	14.10	
20	11.55	433
40	9.30	454
73	7.20	400
109	5.25	394
142	3.70	409
178	2.30	443

TABLE XVIII

$K_4Fe(CN)_6$ in gm.	After-effect $K \cdot 10^6$
0.0132	Decreasing rate
0.0396	414
0.0660	597
0.1320	925
0.2640	1419

These results have been illustrated in Fig 1, curve 'A'. They show that except when a very small amount of ferrocyanide is used, the velocity constants are uniform and higher than in the experiments in which no ferrocyanide is used to an extent depending upon its concentration.

Variation of the End Solution with Constant Amount of Ferrocyanide

In the following experiments the amount of potassium ferrocyanide was kept constant (0.0660 gm) and the amount of the end solution was varied. The results have been graphically shown in Fig 2, curve 'B', and summarised below.

TABLE XIX

Nitroprusside in end solution in gm	After-effect $K \cdot 10^6$
0.0015	169
0.0025	288
0.0050	366
0.0100	597
0.0150	689
0.0200	815

The results show that for a fixed amount of ferrocyanide the rate of decomposition is higher, the greater the amount of the end solution.

Reproduction of the Photochemical After-effect in the Dark

Previous investigation of the photochemical after-effect in $H_2O_2-K_4Fe(CN)_6$ reaction by the author (*loc. cit.*) has shown that the photoformation of potassium aquopentacyanoferrite from aqueous potassium

ferrocyanide causes the phenomenon. It was only natural to suppose that sodium nitroprusside on insolation produces a similar or identical product, which continues to exert its influence even after darkening. It was, therefore, thought desirable to study the decomposition of hydrogen peroxide in presence of sodium aquopentacyanoferrate and unisolated nitroprusside. Sodium aquopentacyanoferrite was prepared in the laboratory by the method of Hofmann (1900) It was oxidised with hydrogen peroxide, and sodium aquopentacyanoferrate of violet colour was obtained in required amounts.

In the following experiments, 0.0010 gm of sodium aquopentacyanoferrite was oxidised with hydrogen peroxide. The oxidation was quick, and when all the peroxide had decomposed, the aquopentacyanoferrate so formed was added to unisolated nitroprusside solution (0.0100 gm) and hydrogen peroxide, both in presence and absence of potassium ferrocyanide.

TABLE XX

Without ferrocyanide

<i>t</i>	<i>a-x</i>	K 10 ⁴
0	14.80	
12	14.60	49
26	13.60	142
35.5	12.90	168
51	11.45	219
72	8.90	307
115	6.00	341

TABLE XXI

$K_4Fe(CN)_6 = 0.0660$ gm.

<i>t</i>	<i>a-x</i>	K. 10 ⁴
0	14.00	
9	11.80	825
23	8.80	877
34.5	7.25	826
49	5.70	796
66	4.10	808
109	1.50	890

The concentration of sodium aquopentacyanoferrate in the following experiments was 2.5 times the concentration employed above.

With higher concentrations of ferrocyanide, uniform velocity constants were obtained. The following are the results (Table XXIII).

TABLE XXII

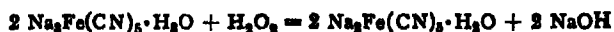
$K_4Fe(CN)_6 = 0.0132$ gm

<i>t</i>	<i>a-x</i>	K 10 ⁴
0	14.10	
10	11.50	885
22.5	9.90	683
35	8.70	599
51.5	7.50	532
78.5	6.00	473
112	4.60	434
149	3.30	423

TABLE XXIII

$K_4Fe(CN)_6$ in gm.	K 10 ⁴
0.0396	114
0.0660	135

In the above experiments, aquopentacyanoferrate obtained by oxidation of aquopentacyanoferrite, according to the reaction



contains alkali. It was feared that these traces of alkali might react with nitroprusside and vitiate the results. It was, therefore, thought necessary to prepare pure sodium aquopentacyanoferrate, from sodium nitroprusside, caustic soda and bromine according to the method of Hofmann (*loc cit.*). The blue violet powder so obtained was used with unisolated nitroprusside and the following results were obtained. The amounts of sodium aquopentacyanoferrate and sodium nitroprusside in 50 c.c. of the reaction mixture were 0.0010 gm. and 0.0100 gm. respectively.

TABLE XXIV

Without ferrocyanide

<i>t</i>	<i>a - x</i>	K 10 ⁵
0	9.70	
40	9.40	34
80	8.30	85
93	7.60	114
108	7.05	128
135	6.10	149

TABLE XXV

$K_4\text{Fe}(\text{CN})_6 = 0.0660 \text{ gm}$

<i>t</i>	<i>a - x</i>	K 10 ⁴
0	9.05	
7	8.00	76
16	7.10	66
30	6.00	60
51	4.60	58
85	2.90	58
115	1.80	61

TABLE XXVI

Heated ferrate-nitroprusside-ferrocyanide mixture to 90° C, cooled and added to H₂O₂ K₄Fe(CN)₆ = 0.0660 gm

<i>t</i>	<i>a - x</i>	K 10 ⁴
0	9.10	
18	8.95	4
55	8.70	4
97	8.00	6
121	7.70	6

It is clear that the reaction with a mixture of aquoferrate and nitroprusside is autocatalytic as already seen in the above experiments. An excess of ferrocyanide regulates the reaction, and gives considerably higher velocity constants. These results show that unisolated nitroprusside-aquopentacyanoferrate mixture qualitatively reproduces the results obtained with isolated nitroprusside. The effect of heat on the unisolated nitroprusside-aquopentacyanoferrate mixture containing ferrocyanide is shown

in Table XXVI. Here also, by heating the above mixture to about 90° C. for a few minutes before adding to hydrogen peroxide, a tremendous fall in the velocity of decomposition is observed. The mixture to which ferrocyanide is added after heating does not show any fall in its catalytic activity. Again, the effect of cyanide ions on the unisolated nitroprusside-aquopentacyanoferrate mixture has been observed to be the same as in the case of pre-insolated nitroprusside, namely, a considerable diminution in the velocity constants. Sodium nitrite, which has been shown to suppress the after-effect almost completely, shows the same retarding effect in this case also. The details are given in Table XXVII. The strength of nitrite was N/100.

Effect of Alkali on H₂O₂-Nitroprusside Dark Reaction

Although the rate of reaction was not measurable in the dark, it was observed that the addition of alkali to the mixture causes a rapid decomposition of hydrogen peroxide, similar to that obtained in pre-insolated nitroprusside-hydrogen peroxide-ferrocyanide mixture. In the following experiment (Table XXVIII), 0.0100 gm of sodium nitroprusside was used, and the strengths of alkali and hydrogen peroxide were N/200 and N/10 respectively. No ferrocyanide was added.

TABLE XXVII

*Treated ferrate-nitroprusside mixture with sodium nitrite and added this mixture to H₂O₂
NaNO₂ = N/100*

<i>t</i>	<i>a - x</i>	<i>K 10⁴</i>
0	6.50	
22	6.40	3
46	6.05	5
88	5.70	6
139	5.15	7
207	4.60	7
242	4.20	8

TABLE XXVIII

<i>t</i>	<i>a - x</i>	<i>K.10⁴</i>
0	14.80	
28	12.40	275
55	10.65	260
81	9.20	255
125	7.10	255
186	4.60	273
235	3.10	289

It is well known that traces of alkali render hydrogen peroxide extremely unstable. In order to test the effect of alkali, therefore, a control experiment was performed using ferrocyanide and sodium hydroxide (0.0660 gm, and N/200 respectively). The resulting velocity constants were almost of the same order as without alkali, although the reaction was slightly autocatalytic. It is, therefore, clear that the amount of alkali employed above does not account for a rapid decomposition of hydrogen peroxide, observed in the foregoing experiment. The end solution was deep yellow.

and gave an emerald green colour with *p*-nitrosodimethylaniline, and a violet colour with nitrosobenzene, indicating the formation of sodium aquopentacyanoferrite. The effect of potassium cyanide on the above mixture was next investigated to see whether a suppression of the decomposition was produced. Mixtures (50 c.c.) of nitroprusside, caustic potash, hydrogen peroxide, and potassium ferrocyanide were prepared, in which the respective strengths were 0.0100 gm., N/200, N/10 and 0.0660 gm. The strength of KCN was N/50.

TABLE XXIX

Without potassium cyanide

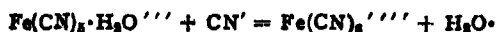
<i>t</i>	<i>a - x</i>	K 10 ⁴
0	14.00	
10	10.40	129
25	6.30	139
38.5	3.70	150
50	2.10	163

TABLE XXX

With potassium cyanide

<i>t</i>	<i>a - x</i>	K 10 ⁴
0	13.30	
5	12.60	47
15	11.60	40
33	9.85	40
64	8.10	34
101	6.90	28
127	6.40	25
160	5.90	22
190	5.60	20

The reaction in presence of ferrocyanide is slightly autocatalytic. When, however, N/50 potassium cyanide is used, a tremendous decrease in the velocity constant is observed and the values show a falling off with time. The explanation is that sodium aquopentacyanoferrite is produced by interaction of alkaline nitroprusside and hydrogen peroxide (Hofmann, *loc cit.*). The aquopentacyanoferrite so formed decomposes hydrogen peroxide at a rapid rate. On the addition of potassium cyanide, the following reaction takes place.—



Aquopentacyanoferrite ions disappear producing ferrocyanide with a concomitant decrease in the velocity constant.

These results are similar to those obtained with pre-insolated nitroprusside-ferrocyanide-cyanide-hydrogen peroxide mixtures, and aquopentacyanoferrate-uninsolated nitroprusside-ferrocyanide-cyanide-hydrogen peroxide mixtures. In view of these observations, the suggestion of Qureshi (*loc cit.*) that colloidal Prussian blue, formed by insolation, causes the after-effect, seems to be untenable. To examine this point, colloidal Prussian blue was prepared in the laboratory by the method of Hofmann, and added to hydrogen peroxide both in presence and absence of ferrocyanide. The

amount of Prussian blue (0.0025 gm) was the same as that of aquopentacyanoferrate used before.

TABLE XXXI

Without $K_4Fe(CN)_6$

<i>t</i>	<i>a - x</i>	$K \cdot 10^7$
0	14.80	
66	14.70	455
132	14.60	447
194	14.50	464
248	14.45	419

TABLE XXXII

$K_4Fe(CN)_6 = 0.0660$ gm.

<i>t</i>	<i>a - x</i>	$K \cdot 10^5$
0	14.80	
65	11.80	151
131	10.90	101
191	10.20	85
247	9.60	76

It is clear that colloidal Prussian blue causes a very slow unimolecular decomposition. In the presence of ferrocyanide, the velocity constants, although higher, show a diminution with time—a behaviour different from that of aquopentacyanoferrate-ferrocyanide-hydrogen peroxide mixture, or pre-insolated nitroprusside-ferrocyanide-hydrogen peroxide mixture. It appears, therefore, that colloidal Prussian blue does not cause the after-effect.

The pre-insolated nitroprusside solutions as well as the end solutions of hydrogen peroxide-nitroprusside insolated mixtures developed a turbidity and showed colloidal particles under the ultramicroscope. An aqueous solution of sodium aquopentacyanoferrate also shows colloidal particles. The effect of colloidal ferric hydroxide was insignificant, indicating that it does not cause the observed after-effect.

Discussion

Qureshi's suggestion (*loc. cit.*) that the photochemical after-effect in the above reaction is due to the formation of colloidal Prussian blue has been experimentally found to be untenable. The latter is produced when aqueous nitroprusside is insolated for a long time, but the results set out above lead to the conclusion that it is not responsible for the after-effect. It is necessary to mention here that preliminary experiments showed that the blue nitroprusside solutions obtained by prolonged insolation gave erratic results, although even in these blue solutions the suggested catalyst, sodium aquopentacyanoferrate, could be chemically detected. Satisfactory results were, however, obtained by employing solutions of nitroprusside which had become pale yellowish brown on insolation and in which no blue tint was noticeable. These observations show that in the initial stage of insolation a new substance is formed which causes the after-effect, and longer exposures lead to the formation of colloidal Prussian blue. The results set out above show

that qualitatively the behaviour of pre-insolated nitroprusside, the pre-insolated mixture of hydrogen peroxide and nitroprusside, and the end solution of pre-insolated mixture of hydrogen peroxide and nitroprusside is identical with that of sodium aquopentacyanoferrate and nitroprusside mixture in the dark

A reference to the literature on the action of light on nitroprusside shows that the formation of colloidal Prussian blue has been taken to be the result of insolation. According to Overbeck, sodium nitroprusside decomposes slowly in sunlight, yielding NO and $\text{Fe}_7(\text{CN})_{18}$. The latter corresponds to Prussian blue, $\text{Fe}_4^{\text{III}}(\text{Fe}^{\text{II}}\text{CN}_6)_3$. On the other hand, Justin-Mueller (1935) says that when exposed to sunlight in an open vessel, an aqueous solution of sodium nitroprusside is decomposed giving NaNO_3 , HCN and $\text{Na}_2\text{Fe}_2(\text{CN})_6$. The last named, in the presence of caustic soda, is converted into Prussian blue. When nitroprusside is exposed to sunlight in a closed vessel, nitric oxide is evolved. It has, however, been observed by the present author that the initial colour change in a dilute aqueous solution of nitroprusside during insolation, from brownish red to a pale yellowish brown, is accompanied by the formation of sodium aquopentacyanoferrate. The latter can be identified by several tests. This substance is formed within 5 to 10 minutes when direct sunlight is used. A longer exposure produces in addition to sodium aquopentacyanoferrate, colloidal Prussian blue.

The catalyst which causes the after-effect has been found to be sodium aquopentacyanoferrate. Several tests are available to detect the formation of sodium aquopentacyanoferrate in a pre-insolated solution of nitroprusside. The latter was mixed with a little dilute aqueous solution of *p*-nitrosodimethylaniline, when a yellow solution was obtained. A little ferrocyanide was added to this mixture in the dark, when an emerald green colouration at once developed. This indicates that ferrocyanide converts aquopentacyanoferrate into aquopentacyanoferrite which is known to react with *p*-nitrosodimethylaniline giving a green colour (Baudisch, 1921). A green colour is also developed in the above mixture when *p*-nitrosodimethylaniline is replaced by dilute sulphuric acid. A direct test for aquopentacyanoferrate is furnished by the starch-iodide reaction. Hofmann (*loc. cit.*) has shown that the former liberates iodine from potassium iodide. A pre-insolated nitroprusside solution was mixed with a little iodide and starch, when a blue iodide of starch was formed. This colour was discharged by thio-sulphate. Another reagent which shows that the pre-illuminated pale yellowish brown solution of sodium nitroprusside contains some sodium aquopentacyanoferrate is nitrosobenzene. A little aqueous solution of the sparingly soluble nitrosobenzene was mixed in the dark with pre-insolated

nitroprusside, and then a freshly prepared solution of potassium ferrocyanide was added, when a violet colour was immediately formed. This colour is given by aquopentacyanoferrite, or aquopentacyanoferrate containing some ferrocyanide. This reagent gives a clear indication of the presence of aquopentacyanoferrate in solutions of nitroprusside which have been insolated for 5 to 10 minutes in direct sunlight. It is significant that these tests are not given by mixtures of pre-insolated nitroprusside and ferrocyanide, which have been heated to about 90° C in the dark for a few minutes before the addition of the enumerated reagents. An alcoholic solution of guaiacum produces a blue colouration with pre-insolated nitroprusside, and the same blue colour is formed with sodium aquopentacyanoferrate. Unilluminated nitroprusside solutions do not give any of these tests, neither does colloidal Prussian blue answer them. It is thus evident that the mechanism of the photochemical after-effect consists in the formation of sodium aquopentacyanoferrate from sodium nitroprusside in light —



The aquopentacyanoferrate ions cause catalytic decomposition after darkening as revealed by the after-effect. The autocatalytic nature of the decomposition in the after reaction is reproduced in the dark by aquopentacyanoferrate-uninsolated nitroprusside mixture.

The effect of ferrocyanide in regulating the reaction and producing a high velocity of decomposition follows from the following scheme —

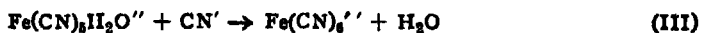


Highly reactive aquopentacyanoferrite is produced by interaction of ferrocyanide and aquopentacyanoferrate contained in pre-insolated nitroprusside. In presence of an excess of ferrocyanide, the amount of aquopentacyanoferrite is kept constant and at a high level, to an extent depending upon the concentration of the former. From this it is clear why a uniformly high velocity is obtained in the presence of an excess of ferrocyanide. When smaller amounts of ferrocyanide are used, the velocity constants show a falling off with the progress of the reaction, as the former ions are gradually oxidised, and the equilibrium reaction shifts to the left with a decrease in the concentration of aquopentacyanoferrite ions. It is clear why ferricyanide is not effective in maintaining a rapid rate of decomposition.

Sodium aquopentacyanoferrate is comparatively stable towards heat, whereas sodium aquopentacyanoferrite undergoes a slow spontaneous change in the dark at room temperature. This change is considerably accelerated by heat. This explains why pre-insolated nitroprusside, heated and added

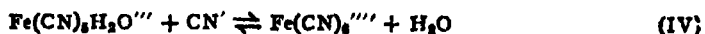
to hydrogen peroxide, does not show lowered reactivity. When a mixture of pre-insolated nitroprusside and ferrocyanide is heated to about 90° C. for a few minutes and then added to hydrogen peroxide, the activity is noticed to diminish considerably, because of the destruction of aquopentacyanoferrite. The same change continues slowly in the dark, and hence a mixture of pre-insolated nitroprusside and ferrocyanide, kept in the dark for some hours before use, shows a lower rate of decomposition than a freshly prepared mixture.

The effect of cyanide ions in suppressing the photochemical after-effect as well as the reaction performed in presence of aquopentacyanoferrate lends support to the mechanism of the photochemical after-effect outlined above. This 'quenching' effect of cyanide ions is due to the conversion of aquopentacyanoferrate to ferricyanide —



The excess of cyanide ions react with ferricyanide ions to give ferrocyanide ions in the end. The slightly autocatalytic effect noticed in experiments with potassium cyanide is due to the alkali produced by hydrolysis.

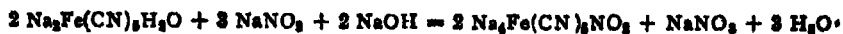
When ferrocyanide is first added to pre-insolated nitroprusside, the formation of aquopentacyanoferrite takes place. This is converted by cyanide ions to ferrocyanide ions —



The effect of sodium nitrite in suppressing the catalytic activity of the pre-insolated solutions of nitroprusside is to be attributed to the formation of nitroprusside by the interaction of nitrite and aquopentacyanoferrite (Hofmann, *loc cit*). The latter is formed when ferrocyanide reacts with aquopentacyanoferrate according to (II). Aquopentacyanoferrite reacts with nitrite as follows —



When nitrite is added to pre-insolated nitroprusside, which has been shown to contain aquopentacyanoferrate, the following reaction takes place.



The quaternary nitroprusside is produced in each case, and as it does not decompose hydrogen peroxide in the dark with a high rate, the photochemical after-effect is 'quenched' by nitrite. It has been seen that aquopentacyanoferrate or aquopentacyanoferrite reacts with nitrite and the resultant solution gives a purple colour with alkali sulphides showing the conversion of the two substances into nitroprusside. The nitrite-treated pre-insolated nitroprusside, containing ferrocyanide, or aquopentacyanoferrite after

treatment with nitrite does not give the characteristic colour tests mentioned previously, showing the complete conversion of aquopentacyanoferrate and aquopentacyanoferrite into nitroprusside

Hofmann (*loc cit*) has shown that aquopentacyanoferrite is formed when alkaline nitroprusside reacts with hydrogen peroxide. That the addition of alkali to hydrogen peroxide-uninsolated nitroprusside mixture in the presence of ferrocyanide reproduces the photochemical after-effect qualitatively in the dark, and further that the cyanide ions suppress this activity, show that aquopentacyanoferrate causes the after-effect. This furnishes further evidence in support of the mechanism involving the photo-formation of aquopentacyanoferrate from nitroprusside.

The author desires to express his best thanks to Prof P S MacMahon for his kind interest in the work. His thanks are also due to the Lucknow University for the grant of a research fellowship which enabled him to carry out this investigation.

Summary

The photochemical after-effect in the reaction between hydrogen peroxide and sodium nitroprusside is due to the photo-formation of sodium aquopentacyanoferrate. The formation of aquopentacyanoferrate in pre-insolated nitroprusside solution has been proved by qualitative tests. Colloidal Prussian blue does not cause the after-effect.

Pre-insolated nitroprusside continues to react in the dark in the manner indicated by the after-effect. Addition of ferrocyanide causes the reduction of aquopentacyanoferrate to aquopentacyanoferrite, which decomposes hydrogen peroxide with a high velocity. The validity of the suggested mechanism for the after reaction has been tested by the effect of potassium cyanide and sodium nitrite, which have been shown to suppress the after-effect by converting aquopentacyanoferrate to ferrocyanide and nitroprusside respectively. Sodium aquopentacyanoferrate, prepared in the laboratory and added to hydrogen peroxide-uninsolated nitroprusside mixture in the dark in presence and absence of ferrocyanide, has been shown to reproduce the observations obtained by insolation.

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IDEAL THEORY IN BOOLEAN ALGEBRA AND ITS APPLICATION TO DEDUCTIVE SYSTEMS

BY MISS S PANKAJAM

(University of Madras)

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THE Ideal Theory of the Distributive Lattice and Boolean Rings was initiated by A Tarski* and developed by M H Stone† who in one of his papers points out that Tarski's 'Deductive Systems' are in fact identical with the additive ideals in the Boolean Algebra of propositions.

In this paper a more detailed study of Ideal Theory of the Boolean Algebra is made with the special object of elucidating the series of concepts and theorems which Tarski advances without proof in his paper*. My treatment of the above involves some new ideas (like Boolean-complements‡ of ideals) and in the proofs I make use of the concepts 'Comprincipal Ideals' and 'Cut-Complements' which have been introduced by Dr Vaidyanathaswamy§ in a recent paper. Thus, the present paper which is devoted to a rapid survey of Ideal Theory in a distributive lattice and in a boolean algebra, it is shown that the notion of the product-complement can be expressed in terms of the Cut-complement and boolean-complement. A continuation of this paper will deal with the application of ideal theory to deductive systems and show incidentally that Tarski's observation that even though the original calculus of propositions may be boolean in nature, yet the structure of deductive systems in that calculus departs from the classical type and conforms to that of Intuitionistic Logic, follows from the fact that the negation¶ of deductive systems corresponds to the product-complement in a distributive lattice whereas the negation of a proposition corresponds to its boolean complement.

* See A Tarski, Bibliography

† M. H Stone (1) See also M H Stone (2). Bibliography

‡ We notice that these boolean-complements are different from the Ortho-complements of M. H Stone (see M H Stone 3) which are simply product-complements in a boolean ring.

§ R Vaidyanathaswamy Bibliography

I take this opportunity of expressing my indebtedness to the departmental lectures on "Lattice Theory" recently delivered by Dr. Vaidyanathaswamy (University of Madras).

¶ See A Tarski. Bibliography.

1. *Ideals in a Distributive Lattice L with 0 and 1*

Definition 1 An α -ideal (A_α) is defined as a set of elements of L such that (1) $x \cdot y \in A_\alpha$ whenever $x \in A_\alpha, y \in A_\alpha$ (we read $x \cdot y$ is in A_α whenever x, y belong to A_α); (2) $x + z \in A_\alpha$ whenever $x \in A_\alpha, z \in L$ or alternatively if $x \in A_\alpha$ then all elements $> x$ are in A_α .

Definition 2 A μ -ideal (A_μ) is a set of elements such that (1) $x + y \in A_\mu$ whenever $x \in A_\mu, y \in A_\mu$, (2) $x \cdot z \in A_\mu$ whenever $x \in A_\mu, z \in L$ or alternatively if $x \in A_\mu$, then all elements $< x$ are in A_μ .

Definition 3 If x, y be any two elements of L, then the set of elements $> x$ is easily seen to be an α -ideal which we call the *principal α -ideal defined by x* [denoted by $P_\alpha(x)$], while the set of elements $< y$ is the *principal μ -ideal $P_\mu(y)$ defined by y*

THEOREM 1 The α -ideal (μ -ideal*) generated by any sub-set S in L (in other words the smallest α -ideal (μ -ideal) containing S) is the set of elements S_α (S_μ) greater than some finite product, say $S, S, S_k \dots S_m$ (less than some finite sum, say $S_i + S_j + S_k + \dots + S_m$) of the elements of the given set S.

For, in the first place it is clear that all such elements constitute an α -ideal S_α . Next by def 1 since any α -ideal A which contains S_α must also contain every finite product $S, S, S_k \dots S_m$ of elements of S_α and therefore also any element greater than such a finite product, it follows $A > S_\alpha$ or S_α is the smallest α -ideal which contains S (Clearly every α -ideal contains 1 and every μ -ideal contains 0)

Definition 4 The sum of a family of α -ideals (μ -ideals) is defined as the α -ideal (μ -ideal) generated by their set-sum

THEOREM 2 The sum of a family $\{A, B, C, \dots\}$ of α -ideals (μ -ideals) is identical with the set of finite products (sums) of elements chosen one from each of the several α -ideals (μ -ideals)

For, $\{A, B, C, \dots\}$ being a family of α -ideals, every finite product of elements chosen from A, B, C, \dots is evidently $>$ than itself and therefore belongs to the ideal generated by $S = \{A, B, C, \dots\}$. On the other hand, every element t of the ideal generated by $S = \{A, B, C, \dots\}$ can be expressed as such as product; for since by Theorem 1, $t > x_1 \cdot x_2 \cdot \dots \cdot x_m$ (where each x belongs to some A) we have $t = t + x_1 \cdot x_2 \cdot \dots \cdot x_m = \pi(t + x_i)$ by the distributive law. Hence since $t + x_i$ belongs to the same α -ideal as x_i , it

* Substitution of words within brackets give dual theorems for μ -ideals. As the proofs of the latter are exactly similar to the theorems for α -ideals, we prove only the former. In general, we shall denote α -ideals by capital letters, the suffixes being used only when required to distinguish them from μ -ideals. The letter P is used to denote principal ideals.

follows that any element t of S can be expressed as a finite product of elements chosen from the α -ideals A, B, C, \dots . Hence the theorem

THEOREM 3 *The set K of the common elements of a family $\{A, B, C, \dots\}$ of α -ideals (μ -ideals) is an α -ideal (μ -ideal).*

($NB - K_\alpha$ is not null since it contains 1)

The proof immediately follows from def 1 and 2. Thus if k_1, k_2 be common elements of A, B, C, \dots then $k_1 k_2$ is also a common element and therefore belongs to K_α . Again, any element $> k_1$ is also an element of each of the ideals A, B, C, \dots and hence of K_α . Hence by def 1, the set K is an α -ideal. We call K the *product* of the family of α -ideals (μ -ideals).

THEOREM 4 *The product of two α -ideals (μ -ideals) is identical with the set of sums (products) of pairs of elements chosen from the two α -ideals (μ -ideals) respectively*

For, if A, B be two α -ideals, then every sum of elements chosen from A, B respectively is a common element of the two ideals, also if t is a common element, then since $t \in A, t \in B, t = t + t$ and thus every common element of A, B can be expressed as a sum of elements chosen from them. Hence the theorem.

Corollary *The product of any family of α -ideals (μ -ideals) is the set of existing sums (products) of the elements chosen one from each of the α -ideals (μ -ideals)*

($NB -$ The product is non-null since it contains 0)

For, every such existing sum is evidently a common element of the family of α -ideals. Conversely, if t be a common element, then it can be expressed as the sum $(t + t + \dots)$ of elements chosen from them.

It may be noticed that when the ideals are principal the sum and product (which we have defined) of a finite* number of the α - (μ -) ideals conforms to the *lattice-sum* and the *lattice-product* of the elements determining them, thus.—

$$\begin{aligned} P_\alpha(x) + P_\alpha(y) + P_\alpha(z) + \dots + P_\alpha(k) &= P_\alpha(x \cdot y \cdot z \cdot \dots \cdot k) \\ P_\mu(x) + P_\mu(y) + P_\mu(z) + \dots + P_\mu(k) &= P_\mu(x + y + z + \dots + k) \\ P_\alpha(x) \cdot P_\alpha(y) \cdot P_\alpha(z) \cdot \dots \cdot P_\alpha(k) &= P_\alpha(x + y + z + \dots + k) \\ P_\mu(x) \cdot P_\mu(y) \cdot P_\mu(z) \cdot \dots \cdot P_\mu(k) &= P_\mu(x \cdot y \cdot z \cdot \dots \cdot k). \end{aligned}$$

* Even when the infinite product a, b, c, \dots exists and $= k$, it is not necessary that the sum (which always exists by theorem 6) of the principal α -ideals $P_\alpha(a), P_\alpha(b), \dots$ should be $= P_\alpha(k)$; for if such were the case, then any convergent ideal would be principal—which is incorrect (see Theorem 29)

It is easily seen that *an ideal A is the sum of all the principal ideals contained in A*. For, if ϕ be the sum of all the principal ideals contained in A, it is clear that $A > \phi$. But if $x \in A$, then $P(x) < A$ by hypothesis and therefore $P(x) < \phi$. Hence x is contained in ϕ and therefore any element of A is contained in ϕ , i.e., $A < \phi$. Hence $A = \phi$.

2.1 Structure of the set of α - and μ -ideals in L

The totality of the α - and μ -ideals form partially ordered systems L_α , L_μ respectively under the ordering relation of 'set-inclusion' ($<$) which is reflexive, transitive and binary. As noticed before for sums and products, this ordering relation conforms to that in L when the ideals are principal. Thus $P_\alpha(x) > P_\alpha(y)$ and $P_\mu(x) < P_\mu(y)$ when and only when $x < y$. The structure of the sets of α - and μ -ideals in L is seen from the following theorems (viz., Theorems 6, 7, 11)

THEOREM 6 L_α , L_μ are complete lattices, i.e., lattices in which unrestricted products and sums exist

For, we have shown (Theorems 2, 4) that the sum (product) of a family of ideals is the smallest ideal which contains every ideal of the family (the largest ideal contained in every ideal); therefore the sums and products of any family of ideals which we have defined are lattice-sums and lattice-products respectively (The 0 of L_α and L_μ is the α -ideal constituted by the element 1 and the μ -ideal constituted by the element 0 respectively, while in both cases, 1 is the whole lattice which is an α - as well as a μ -ideal)*

THEOREM 7 L_α , L_μ are complete lattices with completely distributive sums

Proof Let A_i (where i is an ordinal varying over all ordinals $<$ a fixed ordinal γ) be a family of α -ideals in L. Then clearly, $A \Sigma A_i > \Sigma A_i$, so that we have only to show that $A \Sigma A_i < \Sigma A_i$, i.e., to show that any element of $A \Sigma A_i$ is an element of the ΣA_i . Now (by Theorem 4) the general element of the $A \Sigma A_i$ is a sum of an element x of A and an element of ΣA_i , i.e., it is of the form $x + y_1 y_2 \dots y_m$,—where the y 's are elements of the different A_i 's, this by the distributive law $= (x + y_1)(x + y_2) \dots (x + y_m)$ and since (by Theorem 4) the sums $x + y_i$ belong to the products $A \cdot A_i$, the finite product $\prod (x + y_i)$ is (by Theorem 4) an element of $\Sigma A \cdot A_i$. Hence the theorem

* We notice that when 0 occurs in an equation containing α -ideals it means the α -ideal constituted by the element 1 only, while the 0 occurring in an expression consisting of μ -ideals is the ideal constituted by 0 only.

Corollary. All finite sums are distributive and hence* all finite products are distributive so that L_a, L_μ are distributive lattices which are complete and possess completely distributive sums.

2.2 Product-Complements† in a Distributive Lattice L with 0 and 1

Definition 5 The *product-complement* (*sum-complement*) of an element a is defined as an element a' such that $a \cdot a' = 0$ ($a + a' = 1$) and for all x , $a \cdot x = 0 \supset x < a'$ ($a + x = 1 \supset x > a'$)

[If the product-complement (sum-complement) exists, it is necessarily unique]

Follow some important properties of product-complements

THEOREM 8. $a < b$ implies $A' > B'$

For, since $b \cdot b' = 0$ and $a < b$, $a \cdot b' < b \cdot b' = 0$ or $a \cdot b' = 0$ whence (by def. 5) $b' < a'$ or $a' > b'$.

THEOREM 9 (i) $A < A''$; (ii) $a''' = a'$.

(i) Since $a \cdot a' = 0$, $a < a''$.

(ii) Substituting a' for a in (i) we have $a' < a'''$; again, putting $b = a''$ in Theorem 8, we obtain $a''' > a'$ so that $a''' = a'$

THEOREM 10 If Σa exists, then $\Pi a'$ exists and $= (\Sigma a)'$.

For, since $\Sigma a > a$, $(\Sigma a)' < a'$ (from Theorem 8) for every a in the sum; but if an element is $<$ any a' , it must be $<$ the product-complement of the totality of the a 's, i.e., $< (\Sigma a)'$. For, let $x < a'$; then (from Theorem 8, 9 (i) respectively) $x' > a'' > a$ so that $x' > a$. Hence, $x' > \Sigma a$ implies $x' < (\Sigma a)'$ which together with $x < x''$ implies $x < (\Sigma a)'$. Therefore $(\Sigma a)'$ is by def. 5 the product $\Pi a'$

(When there are only two elements, $(a + b)' = a' \cdot b'$).

We remark the dual of the above property, viz, if Πa exists, then $\Sigma a'$ exists and $= (\Pi a)'$ is not true for the general lattice but can be shown to be valid when L becomes a boolean algebra B

THEOREM 11. Each element of a complete lattice (in particular L_a or L_μ) with completely distributive sums possesses a product-complement.

* However in a complete lattice the distributivity of infinite products do not follow from the distributivity of all sums. See H. M. MacNeille Bibliography.

† For a more detailed treatment of product-complement, Simple and Normal elements in a distributive lattice, see MacNeille (Bibliography), or my paper entitled "On the Formal Structure of the Propositional Calculus—1," to appear shortly in the *Journal of the Indian Mathematical Society*.

Proof. For, since the product and sum of all elements (which exists by the hypothesis that the lattice is complete) are 0 and 1 of the lattice, it is clear that a complete lattice contains both 0 and 1. Now, the set S_x of all elements x such that $a \cdot x = 0$ is not null (since $x = 0$ is such an element) and the sum $a' = \sum x$ of all such elements exists since the lattice is complete, this sum being distributive by hypothesis, $a \cdot a' = a \cdot \sum x = \sum a \cdot x = 0$. Further (by def 5), since a' is the sum of all the x 's in question, $a \cdot x = 0$ implies $x < a'$. Thus a' is the product-complement of a .

It follows that in particular (by Theorems 6, 7) every α - or μ -ideal in a distributive lattice L has a product-complement which is an α - or μ -ideal respectively.

When the ideals are principal, we have

THEOREM 12 *If a, a' are sum-complements (product-complements) in L , then the principal α -ideals (μ -ideals) defined by a, a' are product-complements in L_α (L_μ) and the converse.*

For, let a, a' be sum-complements in L so that $P_\alpha(a) \times P_\alpha(a') = P_\alpha(a + a') = P_\alpha(1) = 0$. Again if X is an arbitrary α -ideal, such that $X \times P_\alpha(a) = 0$, then for every element $x \in X$, $a + x = 1$. Thus (by definition of sum-complements) $x > a'$. Therefore $x \in P_\alpha(a')$. Since this is true for every element x , $X \subseteq P_\alpha(a')$ so that $P_\alpha(a')$ is the product-complement of $P_\alpha(a)$.

2.3. Simple and Normal Elements in L

In a lattice in which every element a has a product-complement a' , we have the following.

Definition 6 The element a is said to be *normal* if $a'' = a$ and it is said to be *simple* if $a + a' = 1$.

THEOREM 13. *Every simple element in L is a normal element*

For, if a is simple, then $a + a' = 1$ so that $a'' = a'' \cdot (a + a') = a \cdot a''$ or $a'' < a$; but since $a'' > a$, we have $a'' = a$.

THEOREM 14. *Sums, products and product-complements of simple elements are simple; if a, b are simple, then $(a \cdot b)' = a' + b'$.*

(The proofs are immediate by simple algebraic manipulations.)

THEOREM 15. *The set of normal elements is identical with the set of product-complements.*

For, if $a = a''$ then a is the product-complement of a' ; and if b' is the product-complement of b , then $b' = b''' = (b')''$ so that any product-complement is normal.

THEOREM 16 a is normal if and only if $a' < b$ implies $a > b'$ for all b or $a' < b'$ implies $a > b$ for all b .

For, if $a = a''$, then $a' < b$ implies $a'' > b'$ which implies $a > b'$, again $a' < b'$ implies $a'' > b''$ which implies $a > b$

If $a + a''$, on putting $b = a'$, $b = a''$ respectively, the implications are seen to be false.

THEOREM 17 $(a \cdot b)'$ is the smallest normal ideal containing a' and b' .

For, if $a' = b'$ then $a \cdot x = 0$ implies and is implied by $b \cdot x = 0$ and vice versa. Hence since x is arbitrary, $ac \cdot x = 0$ implies and is implied by $bc \cdot x = 0$ whence we have $(ac)' = (bc)'$. So that $a' = b'$ implies $(ac)' = (bc)'$. Next if $a' = b'$, $c' = d'$, then clearly $(ac)' = (bc)' = (bd)'$. Therefore since $a' = a'''$, $b' = b'''$, we have $(ab)' = (a'' b'')' = (a' + b')''$. But $(a' + b')''$ is a normal element $> a'$ and $> b'$, and if n is a normal element $> a'$ and $> b'$ then n must be $>$ than $a' + b'$ so that $n = n'' > (a' + b')''$. Hence, $(a b)'$ is the smallest normal element containing a' and b' .

3 0 The Theory of α - and μ -ideals in a Boolean Algebra

We next proceed to study the nature of the lattices B_α , B_μ when the distributive lattice L becomes a boolean algebra B . The conditions for a distributive lattice L to be a boolean algebra B are (1) every element a possesses a product-complement* a' , (2) every element is simple and therefore normal (consequently both the equations $(a + b)' = a' \cdot b'$ and $(a b)' = a' + b'$ are valid in B). Therefore, the boolean complement a' of a is both the sum and product-complement of a so that the principal ideals $P_\alpha(a)$, $P_\alpha(a')$, $[(P_\mu(a), P_\mu(a'))]$ are product-complements in B_α (B_μ). (See Theorem 12)

Definition 7 An ideal A in the lattice of ideals is said to be *neutral* if (A) is distributed by every product

Definition 8. The intersection of any family of principal ideals is called a *comprincipal ideal* †

The characteristic features of the ideal theory of B as contrasted with that of the general distributive lattice L are three, namely.

* From Theorem 11, evidently B_α , B_μ necessarily possess product-complements.

† This concept and that of the cut-complement (see Theorem 22) defined for partially ordered sets by Dr Vaidyanathaswamy, are equally valid for distributive lattices and hence also for boolean algebras

(1) *The set of *simple* ideals is identical with the set of *principal* ideals (Theorem 19).

(2) *The set of *normal* ideals is identical with the set of *comprincipal* ideals (Theorem 25)

(3) The set of *principal* ideals is identical with the set of *neutral* ideals (Theorems 26, 27)

3.1 Boolean Complements, Simple and Principal Ideals

THEOREM 18 *The set \bar{A} of (boolean) complements of elements of an α -ideal A (μ -ideal A) constitutes a μ -ideal (α -ideal) which we call the boolean-complement of the ideal A*

For, if x, y be two elements of an α -ideal (A_α) and x', y' their boolean complements, then since B is a boolean algebra, $x' + y' = (x \cdot y)'$. But since $x \cdot y \in A_\alpha$, $x' + y' = (x \cdot y)' \in \bar{A}$. Further if $k < x'$ then $k' > x'' > x$ and therefore $k' \in A$. Hence, $k = k' (< x') \in \bar{A}$, so that \bar{A} is a μ -ideal

Corollary (i) $\bar{\bar{A}} = A, \bar{\bar{\bar{A}}} = \bar{A}$

The relation between an ideal A and its boolean-complement \bar{A} is obviously a symmetrical one since each consists of the boolean-complements of all the elements of the other. Therefore, $A = \bar{\bar{A}}$. And since $A = \bar{\bar{A}}, \bar{A} = \bar{\bar{\bar{A}}}$.

Corollary (ii) $\overline{P_\alpha(a)} = P_\mu(a'), \overline{P_\mu(a)} = P_\alpha(a')$

Corollary (iii) $\Sigma \bar{A} = \Sigma \bar{A}, \Pi \bar{A} = \Pi \bar{A}$

Proof. We assume the A 's to be α -ideals so that their boolean-complements \bar{A} 's are μ -ideals. Now, the general element of $\Sigma \bar{A}$ ($\Pi \bar{A}$) is the boolean complement of an element of ΣA (ΠA) which element (by Theorems 2, 4) is a finite product (sum) of elements chosen from the A 's. Therefore, the general element of $\Sigma \bar{A}$ ($\Pi \bar{A}$) is the boolean-complement of a finite product (sum) of elements chosen from the A 's, i.e., it is a finite sum (product) of the boolean-complements of elements belonging to the A 's so that the general element of $\Sigma \bar{A}$ ($\Pi \bar{A}$) belongs to $\Sigma \bar{A}$ ($\Pi \bar{A}$). Conversely, it can be

* M H Stone's characterisations of totally additive and totally multiplicative boolean rings [see M H Stone (3)] may be easily derived from these theorems. Thus a totally additive boolean ring must have a unit and is therefore a boolean algebra, and (by Theorem 7) must also be totally multiplicative. Hence, the comprincipal ideals reduce to principal ideals and therefore the normal ideals are identical with principal ideals — which is Stone's characterisation.

Again, a totally multiplicative boolean ring can by adjoining a unit [see M H Stone (2)] be made into a complete boolean algebra and therefore it is easy to deduce Stone's theorem, viz., "principal ideals coincide with normal ideals"

proved in the same way that any element of $\Sigma\bar{A}$ ($\Pi\bar{A}$) is an element of $\Sigma\bar{A}$ ($\Pi\bar{A}$) and hence the corollary

THEOREM 19. *The set of simple ideals in B is identical with the set of principal ideals*

Proof. Considering α -ideals, we prove first that every principal ideal is simple. If a, a' are boolean-complements (by Theorem 12), $P_a(a)$, $P_{a'}(a')$ are product-complements and $P(a) + P(a') = P(a \times a') = P(0) = 1$. Hence any principal ideal $P_a(a)$ is simple. Conversely, to prove that any simple ideal of B is principal, let A be a simple α -ideal and A' its product-complement so that $A + A' = 1$. This implies that any element of the lattice can be expressed as a product of elements chosen from A, A' , therefore there exist $x \in A, y \in A'$ such that $x \cdot y = 0$. If z be an arbitrary element of A , then (by def 5), $z + y = 1$ for all $y \in A'$. Hence $z = z + 0 = z + x \cdot y = (z + x)(z + y) = z + x$ (since $z + y = 1$), i.e., $z > x$. Since this is true for any element z of A , A is the principal α -ideal defined by x .

This theorem can be generalised as follows:

THEOREM 20. *If M, N are two ideals such that $M + N, M \cdot N$ are principal, then M, N are principal*

Proof. Suppose M, N are α -ideals and let $M + N = P(a)$, $M \cdot N = P(b)$. It is shown first that there exist elements x, y ; $x \in M, y \in N$ such that $x \cdot y = a$, $x + y = b$. Now, (by theorems 2, 4) there exist ξ_1, ξ_2 in M, η_1, η_2 in N such that $\xi_1 \cdot \eta_1 = a$, $\xi_2 + \eta_2 = b$. Then, $\xi_1 \xi_2 \cdot \eta_1 \eta_2 < \xi_1 \eta_1 = a$ and $\xi_1 \xi_2 + \eta_1 \eta_2 < (\xi_2 + \eta_2) = b$. But since $\xi_1 \xi_2 \in M, \eta_1 \eta_2 \in N$ (by Theorems 2, 4), $\xi_1 \xi_2 \cdot \eta_1 \eta_2 \in P(a)$; $\xi_1 \xi_2 + \eta_1 \eta_2 \in P(b)$ so that $\xi_1 \xi_2 \cdot \eta_1 \eta_2 = a$; $\xi_1 \xi_2 + \eta_1 \eta_2 = b$. Thus there exist $x = \xi_1 \xi_2$ in $M, y = \eta_1 \eta_2$ in N such that $x \cdot y = a, x + y = b$. Now, if t be an arbitrary element of M , then since $t > a$, $t = t + a = t + x \cdot y = (t + x)(t + y)$. But since $y < (x + y) = b$, $(t + y) < (t + b)$; also since $t + y$ is an element of $M \cdot N = P(b)$, $t + y > b$ and again, $t + y > t$. Therefore, $t + y = t + b$. Hence, $t + y = t + b = t + (x + y) > t + x$, whence $t = (t + x)(t + y) = t + x$ or $t > x$. Since this is true for any element t of M it follows that M is the principal α -ideal defined by x . In the same way, we can show that N is the principal α -ideal defined by y .

3.2. Comprincipal Ideals and Cut-Complements

THEOREM 21. *A comprincipal ideal A is the intersection of all the principal ideals containing it*

For, let the comprincipal ideal A be the intersection of a family (P_i) of principal ideals. Also, let the intersection of all the principal ideals containing A be A' . We have to show that $A = A'$. Clearly, $A' > A$ and

since $A' = \Pi(P_i) \times$ the product of other principal ideals containing A , we have $A' < \Pi(P_i) = A$. Thus the theorem is proved.

Definition 9 Given an ideal A , the *comprincipal envelope* of A is defined as the intersection of all principal ideals containing A

Corollary (i) The comprincipal envelope of A is the smallest comprincipal ideal containing A .

For, a comprincipal ideal K containing A must be the intersection of a family of principal ideals containing A and hence must contain the comprincipal envelope of A which is the intersection of *all* principal ideals containing A

As a consequence of definition (9) and corollary (i), Theorem 21 can be re-stated as follows

Corollary (ii). *A comprincipal ideal is its own comprincipal envelope*

THEOREM 22 *The set A_c of all elements $< (>)$ than every element of an α -ideal A (μ -ideal A) is a comprincipal μ -ideal (α -ideal) which we call the cut-complement of A*

For, if $x \in A_c$, $y \in A_c$ then obviously $x + y \in A_c$ and $x \leq y$ is also in A_c . Thus A_c is a μ -ideal. Further, A_c is comprincipal because it is clearly the intersection of the principal μ -ideals defined by the elements of A

Corollary (i) $(A_c)_c = A_c$ is the comprincipal envelope of A

Since A_{cc} is the cut-complement of A_c it is comprincipal, further (A being an α -ideal) A_{cc} being the cut-complement of A_c , it is the intersection of all the principal α -ideals defined by elements of A_c . But these are precisely the principal α -ideals which contain A . Hence A_{cc} is the intersection of all the principal α -ideals containing A , i.e., it is the comprincipal envelope of A .

Corollary (ii). $A_{cc} = A$ if and only if A is comprincipal

The first part is cor. (ii) of Theorem 21. As for the converse, we have only to observe that if A is not comprincipal, then it cannot be equal to the comprincipal ideal A_{cc}

Corollary (iii). $A_{cc} = A_c$ or the cut-complement of the comprincipal envelope of A is identical with the cut-complement of A .

Putting $A = A_c$ in (ii), we get A_{cc} as the comprincipal envelope of A_c . But A_c , as the cut-complement of A is comprincipal. Therefore (by ii), $A_{cc} = A_c$.

THEOREM 23.* $(\Sigma A)_c = \Pi A_c$.

* The dual of this theorem, namely, $-(\Pi A)_c = \Sigma A_c$ cannot be proved by this method and is not true, we can only show that $(\Pi A)_c \geq \Sigma A_c$.

If the A 's are α -ideals so that A_c 's are μ -ideals, any element of the product $\Pi A_c <$ every element of A , every element of B, \dots and hence $<$ every element of ΣA , so that we have $\Pi A_c < (\Sigma A)_c$. Similarly, any element of $(\Sigma A)_c <$ all elements of (ΣA) and therefore $<$ every element of A , every element of B , etc. Hence, $(\Sigma A)_c < \Pi A_c$ so that $(\Sigma A)_c = \Pi A_c$.

3 3 Relation between the Cut-complement, Boolean-complement and Product-complement

We have defined so far, three operations on ideals in B , viz, boolean-complement, cut-complement and product-complement, the first two change the species of ideals (i.e., α -ideals to μ -ideals and vice versa) while the last preserves the species

The connection between these three operations can be stated thus

THEOREM 24 *The product-complement of an ideal is the cut-complement of its boolean-complement as well as the boolean-complement of its cut-complement [in Symbols, $A' = (\bar{A})_c = (\bar{A}_c)'$]*

Proof Let A be an α -ideal, A its boolean-complement and $(\bar{A})_c$ the cut-complement of A . We have to show that (1) if $x \in A, y \in (\bar{A})_c, x + y = 1$ and (2) if $A \cdot X = 0$ then $X < (\bar{A})_c$. To prove (1), if x' be the boolean-complement of $x (\in A)$ then $x' \in A$ and if $y \in (\bar{A})_c$, then $y >$ every element of \bar{A} so that in particular $y > x'$. Therefore, $y + x > x + x' = 1$, hence $x' + y = 1$ for all x in A and all y in $(\bar{A})_c$ and therefore $A \cdot (\bar{A})_c = 0$. Next to prove (2), if $A \cdot X = 0$ and $x \in X$, then for all $y \in A, x + y = 1$ or $x > y'$ for all $y \in A$. But as y varies in A, y' ranges over all elements of \bar{A} . Therefore $x \in (\bar{A})_c$. Since $x \in X$ is arbitrary, this shows $X < (\bar{A})_c$. Thus $(\bar{A})_c$ is the product-complement of A .

We complete the proof of the theorem by showing that the boolean-complement of the cut-complement of A is identical with the cut-complement of the boolean-complement of A [i.e., $(\bar{A}_c)' = (\bar{A})_c$]. For, the proposition $y \in (\bar{A})_c$ is the proposition $(x) \{x \in A, \sup \cdot y > x'\}$. And the proposition $y \in (\bar{A}_c)'$ is the proposition $y' \in A_c = (x) \{x \in A, \sup \cdot y' < x\}$. But since the proposition $y > x' =$ the proposition $y' < x$, the above two statements are logically equivalent and therefore we have $(\bar{A})_c = (\bar{A}_c)'$.

Corollary (i) Every product-complement is comprincipal and conversely every comprincipal ideal is the product-complement of some ideal.

For, since Theorem 24 exhibits the product-complement of an ideal as the cut-complement of its boolean-complement, it follows (by Theorem 22) that all product-complements are comprincipal. Conversely, if an ideal M is comprincipal, it is the cut-complement of some ideal A (in particular,

by Theorem 22 we can take $A = M_c$ so that (by Theorem 18, cor. 1), $A_c = (\bar{A})_c =$ the product-complement of the ideal \bar{A} by Theorem 24.

*Corollary (ii).** $(\Sigma A)' = \Pi A'$

For, $(\Sigma A)' = (\Sigma \bar{A})_c = (\Sigma A)_c = \Pi (\bar{A})_c = \Pi A'$ (by Theorem 24, cor. (iii) of Theorem 18, Theorem 23 and Theorem 24 respectively)

Corollary (iii). The product of any number of normal elements is normal.

THEOREM 25 *The set of normal ideals is identical with the set of comprincipal ideals*

Proof We have already seen (Theorem 15) that in B_a or B_μ the set of normal elements is identical with the set of product-complements, these product-complements (by cor. (i), Theorem 24) are identical with the set of comprincipal ideals. Hence the set of normal ideals is identical with the set of comprincipal ideal

Corollary A'' is the comprincipal envelope of A

Now, A'' is known to be the smallest normal ideal containing A (or the normal envelope of A), for, in the first place, A'' is a product-complement and therefore normal. And if X be a normal ideal containing A , then $X' < A'$ so that $X = X'' > A''$, therefore, A'' is the smallest comprincipal ideal containing A , i.e., (by cor. (i) of Theorem 21) it is the comprincipal envelope of A .

3.4. Neutral Ideals

THEOREM 26 *Principal Ideals are neutral.*

Proof We have to show that if $P(x)$ is a principal α -ideal and $\{A\}$ any family of α -ideals of which A is a typical member, then

$$P(x) + \Pi(A) = \Pi(P(x) + A)$$

Lemma We first prove that $P(x) + Y$ is identical with the set of elements t such that $(t + x') \in Y$. For, let $x' + t \in Y$. Then since $t + x \in P(x)$ and $(t + x') \in Y$ by hypothesis, it follows that $t = (t + x)(t + x') \in (P(x) + Y)$. Conversely, if $t \in P(x) + Y$ then (by Theorem 2), $t = x_1 a_1$ where $x_1 (> x)$ $\in P(x)$ and $a_1 \in Y$, therefore, $t + x' = x_1 a_1 + x' = (x' + a_1)(x' + x_1) = x' + a_1$ (since $x' + x_1 > x + x' = 1$) $\in Y$. Thus $P(x) + Y$ is the set of all elements t such that $(t + x') \in Y$.

Hence it follows by putting $Y = \Pi(A)$ in the lemma, that $P(x) + \Pi(A)$ is the set $S(t)$ of all elements t such that $(t + x') \in \Pi A$. Therefore this set $S(t)$ is the set-product (and therefore the ideal-product) of the sets $S_\Delta(t)$,

* The dual result, viz., $(\Pi A)' = \Sigma A'$ cannot be obtained for the reason expressed in the f.a. under Theorem 23.

$S_B(t), \dots$ where $S_A(t)$ is the set of elements t such that $(t + x') \in A$, so that by the lemma $S_A(t)$ is identical with the ideal $P(x) + A$. Similarly $S_B(t)$ is identical with $P(x) + B$; etc. Hence, $P(x) + \Pi(A) = \Pi(P(x) + A)$

THEOREM 27 *Neutral Ideals are principal*

Proof. To prove this, it is sufficient to show that if A is not principal, then there exists one product which does not distribute it

Now, any ideal A is the sum of all the principal ideals $(P(x), x \in A)$ contained in it so that (by cor (ii) Theorem 24) $A' = \Pi P(x')$. Hence, $A + \Pi P(x') = A + A' = 1$ (by Theorem 19). But since $A > P(x)$, $[A + P(x')] > [P(x) + P(x')]$ which $= 1$. Hence, $\Pi [A + P(x')] = 1 \neq A + \Pi P(x')$. Thus the product $\Pi P(x')$ does not distribute A , hence the theorem

The following theorem is a consequence of the above two results

THEOREM 28 *$A + D$ is normal for all normal ideals D if and only if A is principal*

Proof First let A be principal. Then since (by Theorems 25, 26, 27 respectively) every normal ideal D is comprincipal (and therefore $=$ a product ΠP of principal ideals) and every principal ideal is neutral, we have $A + D = A + \Pi P = \Pi (A + P)$ which being the product of principal ideals $A + P$, is comprincipal, and therefore (by Theorem 25) normal; so that $A + D$ is normal for all normal ideals D . Conversely, if A is not principal, we can find normal ideals D such that $A + D$ is not normal; e.g., since A is not principal (by Theorem 19) it cannot be simple so that $A + A' \neq 1$. But $(A + A')' = 1$. Hence $A + A'$ is not normal even though A' is normal

3.5 Convergent Ideals

Definition 10 An α -ideal (μ -ideal) is said to be convergent if the product (sum) of all its elements exists

THEOREM 29 * *An ideal A is convergent if and only if any one of the following conditions is satisfied*

- (i) A_c is principal
- (ii) \bar{A} is convergent
- (iii) A' is principal.
- (iv) A'' is principal
- (v) The comprincipal envelope of A is principal
- (vi) $A' + D' = (A \cdot D)'$ for every ideal D .
- (vii) $A'' + D'' = (A + D)''$ for every ideal D

* This theorem *ad verbatim* corresponds to Satz 26 of Tarski's (see A. Tarski).

Proof. As usual, we prove the theorem for α -ideals.

(i) If A be a convergent α -ideal, A_c its cut-complement and if the product of all its elements (which exists by hypothesis) $= K$, then (by Theorem 22) every element of $A_c < K$ and also since $K <$ every element of A , $K \in A_c$, hence A_c is the principal μ -ideal defined by K . *Conversely*, if A_c is principal (say $P_a(k)$) then since $K <$ every element of A and since every element of A_c (in other words every element $<$ every element of A) $< K$, K satisfies def 10 of 'product of all elements of A '. Hence A is convergent.

(ii) Since A is a convergent α -ideal, by def 10 the product (ΠA) of all elements of A exist, and because B is a boolean algebra (according to the remark made at the end of Theorem 10), $\Sigma a'$ exists and $= (\Pi a)'$, hence \bar{A} is convergent. *Conversely*, if A be assumed to be convergent so that Σa exists, then (by the above-mentioned theorem), $\Pi a'$ exists and $= (\Sigma a)'$, therefore A is convergent.

(iii) If A is convergent, then [by (ii)] A is convergent and hence $A' = (\bar{A})_c$ is principal [by (i)], *conversely*, if A' is principal, i.e., (by Theorem 24) $(\bar{A})_c$ is principal, then A_c is principal [by cor (ii), Theorem 18] and hence A is convergent.

(iv) and (v) Since (by corollary of theorem 25) A'' is the comprincipal envelope of A , we have only to show that if A is convergent, A'' is principal and *vice versa*. This is immediately seen, for if A is convergent, then [from (iii)] A' is principal and therefore A'' is principal. *Conversely*, if A'' is principal, then $A' (= A''')$ is principal and hence [from (iii)], A is convergent.

(vi) Let $A' + D' = (A \cdot D)'$ for all D , to show A is convergent. Now (by Theorem 17) $A' + D' = (AD)' = (A' + D')''$ so that $A' + D'$ is normal for all normal ideals D' . Hence (by Theorem 28) A' is principal so that [by (iii)] A is convergent. *Conversely*, if A is convergent, then since A' is principal and D' normal, (by Theorem 28) $A' + D'$ is normal for all D' whence $A' + D' = (A' + D')'' = (AD)'$.

(vii) Given A to be convergent, we have to show $A'' + D'' = (A + D)''$ for all D .

Now, since A is convergent, A' , A'' are [by (iii) and (iv)] principal. Hence since D'' is normal (by Theorem 28), $A'' + D''$ is normal for all D , i.e., $A'' + D'' = (A'' + D'')'' = (A'''D''')' = (A'D')' = (A + D)''$ [by def 6, by Theorem 24, cor. (ii), by Theorem 24, cor. (ii) respectively].

Conversely, if $A'' + D'' = (A + D)''$ for all D , to prove A is convergent

Now, as before $(A + D)' = (A' \cdot D')' = (A''' \cdot D''')' = (A'' + D'')'$ so that we have $(A'' + D'') - (A'' + D'')$ whence $A'' + D''$ is normal for all D , and since D'' is normal (by Theorem 28), A'' is principal, i.e., A is convergent

THEOREM 30 *If A, D are convergent, then $A + D, A \cdot D$ are convergent*

For, since A, D are convergent [by Theorem 29 (iii)], A', D' are principal. Now in order to prove $A + D, A \cdot D$ are convergent, we have to show $(A + D)', (A \cdot D)'$ are principal, which is immediately seen, for by (vi), $(A \cdot D)' = (A' + D')$ which is principal (since A', D' are principal), and again [by Theorem 24, cor (ii)], $(A + D)' - A' \cdot D'$ which is also principal. Hence the theorem

THEOREM 31 *If $A + D$ is principal, $A \cdot D$ is convergent, then A, D are convergent*

Proof. For, a principal ideal contains the comprincipal envelope of any ideal which it contains, hence since $A + D$ is principal it follows (by corollary of Theorem 25) that $A + D > A'', A + D > D''$ so that $A + D > A'' + D''$. But since $A'' > A, D'' > D$ we have $A'' + D'' > A + D$. Hence,

$$A'' + D'' = A + D = \text{a principal ideal} \quad (1)$$

But since (by hypothesis) $A \cdot D$ is convergent, $(A \cdot D)'$ is [by Theorem 29 (iii)] principal, and $(A \cdot D)' = (A'' \cdot D'')' = (\overline{A'' \cdot D''})_c$ (by theorems 17, 24 respectively) so that $(\overline{A'' \cdot D''})_c$ is principal. Therefore, since if the boolean-complement of an ideal is principal the ideal itself is principal, it follows that $(A'' \cdot D'')_c$ is principal. But since $A'' \cdot D''$ is normal, it is comprincipal (by Theorem 25) and also, if the cut-complement of a comprincipal ideal X is principal then [from Theorem 22, cor (ii)] X itself is principal, i.e., $A'' \cdot D''$ is principal. (2)

Therefore from (1) and (2) by Theorem 21, we obtain A'', D'' to be principal and hence [by Theorem 29 (ii)] A, D are convergent

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